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I. *The Reflexion of Long Electromagnetic Waves from the Upper Atmosphere.* *By* D. BURNETT, *M.A., B.Sc., B.A., Carnegie Teaching Fellow in the University of Aberdeen* *.

THE problem of the reflexion of electromagnetic waves from the upper atmosphere has been considered mathematically by Macdonald † in an idealized form, viz., when the earth is a perfectly conducting sphere surrounded by an atmosphere made up of two parts, each homogeneous in itself, separated by a spherical surface concentric with the earth. His solution is satisfactory for short and medium wave-lengths, but not for the very long waves now employed, as the approximations which he makes are not valid in this case unless in the immediate neighbourhood of the transmitter ; whereas modern ideas of the constitution of the upper atmosphere suggest that Macdonald's idealized atmosphere will most closely represent the effect of the actual atmosphere in the case of very long waves, so that it is of some importance to get a solution for this case.

The various correcting factors required in Macdonald's result can be found by considering the second approximations, and these might be useful for getting more accurate results for moderate wave-lengths ; but it has been found that only a slightly greater range of validity is obtained for very long

* Communicated by the Author.

† Proc. Roy. Soc. A, cviii. p. 52 (1925).

waves—for example, with a wave-length of 19 km., Macdonald's result for the first reflected wave is correct up to angular distances of 5° from the transmitter, and the inclusion of the correcting factors gives results up to about 7°. Beyond this point accurate values cannot be found, on account of the asymptotic character of some of the correcting factors; the magnitude of the error can be reduced to a certain minimum value and no further, and the method can be used only when this minimum value is sufficiently small.

Macdonald has also given, in the second part of the paper quoted *, a method of dealing with the cases to which his first method is inapplicable, but it involves the calculation of a large number of integrals, and for very long waves the amount of arithmetic involved seems to be very great; moreover, a factor M_k is assumed constant, and certain other approximations are made which are probably not accurate for very long waves. The method given below, analogous to that used by Macdonald in his discussion of the diffracted wave †, obtains an *exact* result, and the amount of computation required to get numerical values is not excessive, unless near the transmitter—especially as most of the quantities which have to be calculated are functions of the wave-length and of the electric constants of the earth and atmosphere, but not of the distance from the transmitter, and once they are found the results for all distances can quickly be calculated. It has already been noticed that Macdonald's solution is valid near the transmitter, so that the two methods together give a complete solution, except possibly for a band of intermediate distances, and the width of this band can be reduced only by increasing considerably the arithmetic involved in the second method. No solution has yet been obtained suitable for calculating results at these intermediate distances.

It is assumed in the analysis that the earth is perfectly conducting; but the modification required to take account of finite conductivity can easily be made ‡, and calculation has shown that this effect is small—much less than the possible error in present-day experimental work,—so that it can be neglected in the meantime.

The quantity tabulated is the amplitude of the magnetic force in the diffracted wave plus a wave reflected once from the upper atmosphere, expressed as a fraction of the

* *Loc. cit.* p. 70.

† Proc. Roy. Soc. A, xc. p. 50 (1914).

‡ *Cf.* H. M. Macdonald, Proc. Roy. Soc. A, xcii. p. 493 (1916).

amplitude at the same point due to the same transmitter in free space. The diffracted wave is calculated from Macdonald's formula *, with the addition of a correction noted by Watson †, which affects the phase of the result. Macdonald uses the approximation

$$P_n(\cos\theta) = J_0\{(2n+1)\sin\tfrac{1}{2}\theta\}, \qquad (n \text{ large}),$$

which is valid only when $n\theta^3$ is negligibly small. Laplace's approximation, however, viz.,

$$P_n(\cos\theta) = \sqrt{\frac{2}{\pi(n+\frac{1}{2})\sin\theta}}\cos\left\{(n+\tfrac{1}{2})\theta - \frac{\pi}{4}\right\},$$

is adequate, and the correction to Macdonald's result is easily made. The corrected value, with his notation, is

$$\frac{\overline{\psi}}{\overline{\psi}_0} = 4\pi^{1/2}\left(z_0^{1/3}\sin\frac{\theta}{2}\right)^{1/2}\left(\cos\frac{\theta}{2}\right)^{-3/2} e^{\pi i/12 + 2iz_0\left(\sin\frac{\theta}{2} - \frac{\theta}{2}\right)}$$

$$\times\Sigma(3x_k)^{-2/3}e^{-(3x_k)^{2/3}z_0^{1/3}\cdot\frac{1}{2}\theta\cdot e^{\pi i/6}}.$$

The Reflected Waves.

Macdonald's solution for a perfectly conducting spherical earth (radius r_0) surrounded by an ideal atmosphere, as explained above, is in the form

$$\psi = \psi_{00} + \sum_{k=1}^{k=\infty}\psi_{0k},$$

where $\psi = r_0\sin\theta$ times the magnetic force on the surface at an angular distance θ from the source ;

ψ_{00} represents the direct (diffracted) wave ;

and ψ_{0k} represents a wave which has been reflected k times from the upper atmosphere.

The value found for ψ_{0k} is

$$ik^{-1}r_0^{-\frac{1}{2}}3^{-1/3}z_0^{1/3}\pi^{1/2}\sum_{n=0}^{n=\infty}(2n+1)^{3/2}(\sin\theta)^{1/2}$$

$$\sin\left\{(n+\tfrac{1}{2})\theta - \frac{\pi}{4}\right\}\left(\frac{w_1}{\overline{w}_1}\right)^k\frac{\overline{w}_0'^{k-1}}{w_0'^{k+1}}M_k^{\,k},$$

* *Loc. cit.* (1914).

† Proc. Roy. Soc. A, xcv. p. 83 (1918).

so that for the first reflected wave, which alone is considered here,

$$\psi_{01} = i\kappa^{-1} r_0^{-2} 3^{-1/3} z_0^{1/3} \pi^{1/2} \sum_{n=0}^{n=\infty} (2n+1)^{3/2} (\sin\theta)^{1/2} \sin\left\{(n+\tfrac{1}{2})\theta - \frac{\pi}{4}\right\} \mathrm{M}_1 \frac{w_1}{\bar{w}_1} \frac{1}{w_0'^2}, \quad . \quad \text{(A)}$$

where

$$\kappa = \frac{2\pi}{\lambda}, \qquad z_0 = \kappa r_0,$$

$$w_0 = -i\left(\frac{2}{\pi}\right)^{1/2} 3^{-1/6} z_0^{1/6} \zeta_0^{1/3} \mathrm{K}_{1/3}(\zeta_0 e^{-\pi i})$$

$$w_0' = i\left(\frac{2}{\pi}\right)^{1/2} 3^{1/6} z_0^{-1/6} \zeta_0^{2/3} \mathrm{K}_{2/3}(\zeta_0 e^{-\pi i}),$$

$$\zeta_0^{2/3} = \left(\frac{1}{9z_0}\right)^{1/3} (n+\tfrac{1}{2}-z_0),$$

$$\frac{w_1}{\bar{w}_1} = -\frac{\zeta_1^{1/3} \mathrm{K}_{1/3}(\zeta_1 e^{-\pi i})}{\bar{\zeta}_1^{1/3} \mathrm{K}_{1/3}(\bar{\zeta}_1 e^{+\pi i})},$$

$\zeta_1^{1/3}$ and $\bar{\zeta}_1^{1/3}$ being the two square roots of $\left(\frac{1}{9z_1}\right)^{1/3} (n+\frac{1}{2}-z_1)$ with

$$\arg\zeta_1 = \frac{3\pi}{2}, \qquad \arg\bar{\zeta}_1 = -\frac{3\pi}{2}$$

when $n+\frac{1}{2} < z_1$, and $z_1 = \kappa r_1$ where r_1 is the radius of the surface of discontinuity in the atmosphere ; also, if

$$\frac{\kappa_1}{\kappa} = \sqrt{\frac{\mathrm{K}'}{\mathrm{K}}} = \frac{1}{\rho},$$

K being the dielectric constant of the lower, K′ of the upper atmosphere—the permeabilities being supposed unity in both—and $z_{11} = \kappa_1 r_1$, then

$$\mathrm{M}_1 = -\frac{\rho \dfrac{w_{11}'}{w_{11}} - \dfrac{w_1'}{w_1}}{\rho \dfrac{w_{11}'}{w_{11}} - \dfrac{\bar{w}_1'}{\bar{w}_1}},$$

where w_1 and w_{11} are the same functions of z_1 and z_{11} as w_0 is of z_0, and

$$\bar{w}_1 = +i\left(\frac{2}{\pi}\right)^{1/2} 3^{-1/6} z_1^{1/6} \bar{\zeta}_1^{1/3} \mathrm{K}_{1/3}(\bar{\zeta}_1 e^{\pi i}),$$

$$\bar{w}_1' = -i\left(\frac{2}{\pi}\right)^{1/2} 3^{1/6} z_1^{-1/6} \bar{\zeta}_1^{2/3} \mathrm{K}_{2/3}(\bar{\zeta}_1 e^{\pi i}).$$

If $\nu = n + \frac{1}{2} - z_0$, formula (A) can be written

$$\psi_{01} = 2\kappa\pi^{1/2}3^{-1/3}z_0^{-1/6}\left(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\right)^{1/2} e^{-iz_0\theta+\pi i/4}$$

$$\int_{-\infty}^{\infty} d\nu\left(1+\frac{\nu}{z_0}\right)^{3/2} e^{-\nu i\theta}\frac{w_1}{\bar{w}_1}\frac{\mathrm{M}_1}{w_0'^2}$$

$$= -2\kappa\pi^{1/2}e^{-iz_0\theta+\pi i/4}\left(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\right)^{1/2}$$

$$\int_{-\infty}^{\infty} d\nu\left(1+\frac{\nu}{z_0}\right)^{3/2} e^{-\nu i\theta}\frac{\mathrm{M}_1\dfrac{w_1}{\bar{w}_1}}{\zeta_0^{4/3}\mathrm{K}^2_{2/3}(\zeta_0 e^{-\pi i})},$$

and . . . (B)

$$\zeta_0^{2/3} = \left(\frac{1}{9z_0}\right)^{1/3}\cdot 2\nu, \qquad \zeta_1^{2/3} = 2\left(\frac{1}{9z_1}\right)^{1/3}(\nu - z_1 + z_0).$$

When ν is complex and its modulus large $|\zeta_1|$ is also large and $\dfrac{w_1}{\bar{w}_1}$ is approximately $-e^{\zeta_1-\bar{\zeta}_1} = -e^{2\zeta_1}$. The integrand in (B) is an analytic function of ν, and can easily be shown to vanish at infinity in the lower half of the ν plane, *i.e.*, when $\pi < \arg.\ \nu < 2\pi$. The value of the integral is $2\pi i$ times the sum of the residues at the poles, which are the zeros of w_0', $\bar{w}_1$ and the denominator of M_1, and it can be shown that only the zeros of w_0' need be considered.

Macdonald has proved * that all the zeros of $z^{2/3}\mathrm{K}_{2/3}(z)$ whose arguments lie between $-\pi$ and $+2\pi$ are on the line $\arg z = \dfrac{3\pi}{2}$; and it can be proved in the same way that the zeros of $z^{1/3}\mathrm{K}_{1/3}(z)$, with arguments between $-\pi$ and 2π, lie on the same line, so that all the zeros of $\bar{w}_1$, such that $-\pi < \arg\bar{\zeta}_1 e^{\pi i} < 2\pi$, satisfy the condition $\arg\bar{\zeta}_1 + \pi = \dfrac{3\pi}{2}$ or $\arg\bar{\zeta}_1 = \dfrac{\pi}{2}$, and therefore $\arg\zeta_1 = -\dfrac{\pi}{2}$. In this case the Bessel functions in w_1 and $\bar{w}_1$ can be written as $\mathrm{K}_{1/3}(ze^{-3\pi i/2})$ and $\mathrm{K}_{1/3}(ze^{3\pi i/2})$, where z is real and these functions are equal in magnitude but of opposite sign for the same value of z, so that the roots of $\bar{w}_1$ are also roots of w_1. Hence there are no poles of the integrand at the zeros of $\bar{w}_1$.

The zeros of the denominator of M_1 are given by

$$\rho z_{11}^{-1/3}\,\zeta_{11}^{1/3}\frac{\mathrm{K}_{2/3}(\zeta_{11}e^{-\pi i})}{\mathrm{K}_{1/3}(\zeta_{11}e^{-\pi i})} = z_1^{-1/3}\bar{\zeta}_1^{1/3}\frac{\mathrm{K}_{2/3}(\bar{\zeta}_1 e^{\pi i})}{\mathrm{K}_{1/3}(\bar{\zeta}_1 e^{\pi i})},$$

* *Loc. cit.* p. 53 (1914).

and so, if $|\zeta_{11}|$ and $|\zeta_1|$ are not small,

$$\rho z_{11}^{-1/3}\zeta_{11}^{1/3} = z_1^{-1/3}\bar{\zeta}_1^{1/3}$$

approximately, in the neighbourhood of a root, from the asymptotic expansions of the Bessel functions. But in the lower half of the ν plane $\frac{\pi}{2} < \arg\zeta_{11}^{1/3} < \pi$ and $-\frac{\pi}{2} < \arg\bar{\zeta}_1^{1/3} < 0$, and the above relation cannot be satisfied. Since

$$\frac{K_{2/3}(\zeta e^{-\pi i})}{K_{1/3}(\zeta e^{-\pi i})} = 1 - \frac{1}{6\zeta}\cdots$$

asymptotically, it can be inferred that there is no root in that part of the lower half plane for which $6|\zeta_{11}|$ and $6|\bar{\zeta}_1|$ are of order greater than unity. If $|\zeta_{11}|$ is small,

$$\zeta_{11}^{1/3}\frac{K_{2/3}(\zeta_{11}e^{-\pi i})}{K_{1/3}(\zeta_{11}e^{-\pi i})} = \frac{(\frac{1}{2}e^{-\pi i})^{-2/3}}{(\frac{1}{2}e^{-\pi i})^{-1/3}} = 2^{1/3}e^{\quad 3},$$

approximately, while if $|\bar{\zeta}_1|$ is small,

$$\bar{\zeta}_1^{1/3}\frac{K_{2/3}(\bar{\zeta}_1 e^{\pi i})}{K_{1/3}(\bar{\zeta}_1 e^{\pi i})} = 2^{1/3}e^{-\pi i/3}.$$

Hence, if there is a root near $\zeta_{11}=0$, $\arg\bar{\zeta}_1^{1/3}\frac{K_{2/3}(\bar{\zeta}_1 e^{\pi i})}{K_{1/3}(\bar{\zeta}_1 e^{\pi i})}$ must be approximately $\frac{\pi}{3}$ at it, which is seen to be impossible in the lower half plane ; and similarly there can be no root near $\zeta_1=0$ in the lower half plane.

It follows that the integral is equal to $2\pi i$ times the sum of the residues at the zeros of w_0', and these have already been calculated by Macdonald *. To find the residues let

$$\frac{1}{\zeta_0^{4/3}K_{2/3}^2(\zeta_0 e^{-\pi i})} = \sum_{k=0}^{k=\infty}\left\{\frac{A_k}{\nu-\nu_k} + \frac{B_k}{(\nu-\nu_k)^2}\right\},$$

where $\nu=\nu_0, \nu_1\ldots$ are the zeros of $\zeta_0^{2/3}K_{2/3}(\zeta_0 e^{-\pi i})$; then

$$B_k = \operatorname*{Lt}_{\nu=\nu_k}\left\{\frac{\nu-\nu_k}{\zeta_0^{2/3}K_{2/3}(\zeta_0 e^{-\pi i})}\right\}^2 = \frac{z_0}{2\nu_k}\left\{\frac{1}{\zeta_0^{2/3}K_{1/3}(\zeta_0 e^{-\pi i})}\right\}^2_{\nu=\nu_k},$$

which, if $\zeta = xe^{-\pi i/2}$, becomes

$$\frac{z_0}{2\nu_k}\frac{e^{2\pi i/3}}{x_k^{4/3}K_{1/3}^2(x_k e^{-3\pi i/2})} = -\frac{z_0^{2/3}}{3^{2/3}x_k^2 K_{1/3}^2(x_k e^{-3\pi i/2})}.$$

* *Loc. cit.* p. 54 (1914).

Also $$A_k = \underset{\nu=\nu_k}{\text{Lt.}} \frac{\partial}{\partial \nu} \frac{(\nu-\nu_k)^2}{\zeta_0^{4/3} K^2_{2/3}(\zeta_0 e^{-\pi i})},$$

which, after some simplification, reduces to

$$\frac{2 z_0^{1/3}}{3^{4/3}} \frac{e^{\pi i/3}}{x_k^{8/3} K^2_{1/3}(x_k e^{-3\pi i/2})},$$

and so

$$B_k = -\tfrac{1}{2}(3x_k)^{2/3} z_0^{1/3} e^{-\pi i/3} A_k = -\nu_k A_k.$$

Hence

$$\psi_{01} = -3^{-1/3} z_0^{-1/6} (2\pi)^{1/2} \kappa (\sin\theta)^{1/2} e^{\pi i/4 - i z_0 \theta}$$

$$\int_{-\infty} d\nu \left(1+\frac{\nu}{z_0}\right)^{3/2} \frac{e^{-i\nu\theta} \cdot M_1 \frac{w_1}{\bar{w}_1}}{\zeta_0^{4/3} K^2_{2/3}(\zeta_0 e^{-\pi i})}$$

$$= -3^{-1/3} z_0^{-1/6} (2\pi)^{3/2} \kappa (\sin\theta)^{1/2} e^{3\pi i/4 - i z_0 \theta}$$

$$\sum_{k=0} A_k (f - \nu f')_{\nu=\nu_k},$$

where $$f = \left(1+\frac{\nu}{z_0}\right)^{3/2} M_1 \frac{w_1}{\bar{w}_1} e^{-i\nu\theta}$$

and $$\frac{f'}{f} = \frac{3}{2z_0} \frac{1}{1+\frac{\nu}{z_0}} + \frac{1}{M_1} \frac{\partial M_1}{\partial \nu} + \frac{\bar{w}_1}{w_1} \frac{\partial}{\partial \nu} \frac{w_1}{\bar{w}_1} - i\theta.$$

Therefore

$$\psi_{01} = 3^{-1/3} z_0^{-1/6} (2\pi)^{3/2} \kappa (\sin\theta)^{1/2} e^{-\pi i/4 - i z_0 \theta} \Sigma \nu_k A_k f_k (E_k + i\theta),$$

where

$$E_k = \frac{1}{\nu} - \frac{1}{M_1} \frac{\partial M_1}{\partial \nu} - \frac{\bar{w}_1}{w_1} \frac{\partial}{\partial \nu} \frac{w_1}{\bar{w}_1},$$

omitting the term

$$\frac{3}{2z_0} \frac{1}{1+\frac{\nu}{z_0}},$$

which is much smaller than the others. E_k is independent of θ. Also

$$A_k = \frac{2}{3}\left(\frac{z_0}{3}\right)^{1/3} \frac{e^{\pi i/3}}{x_k^{8/3} K^2_{1/3}(x_k e^{3\pi i/2})}$$

$$= \frac{2}{3}\left(\frac{z_0}{3}\right)^{1/3} \frac{e^{\pi i/3}}{x_k^{8/3}} \left[\frac{2\sin\frac{\pi}{3}}{\pi\{I_{-1/3}(x_k e^{-3\pi i/2}) - I_{1/3}(x_k e^{-3\pi i/2})\}}\right]^2$$

$$= \frac{2}{\pi^2}\left(\frac{z_0}{3}\right)^{1/3} \frac{e^{\pi i/3}}{x_k^{8/3}} \frac{1}{\{J_{-1/3}(x_k) + J_{1/3}(x_k)\}^2},$$

using the definitions of the K and I functions*. Hence, if the Hankel function

$$H_{1/3}(x) = He^{ia},$$

so that

$$J_{1/3}(x) = H\cos\alpha, \qquad J_{-1/3}(x) = H\cos\alpha + \frac{\pi}{3},$$

$$A_k = \frac{2}{3\pi^2}\left(\frac{z_0}{3}\right)^{1/3}\frac{e^{\pi i/3}}{x_k^{8/3}}\frac{1}{H_k^2\cos^2\alpha_k + \frac{\pi}{6}}$$

and $$\nu_k A_k = \left(\frac{z_0}{3}\right)^{2/3}\frac{1}{\pi^2 x_k^2}\frac{1}{H_k^2\cos^2\alpha_k + \frac{\pi}{6}},$$

so that

$$\psi_{01} = 12\,.\,\pi^{-1/2}\kappa z_0^{1/2}e^{-\pi i/4 - iz_0\theta}\left(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\right)^{1/2}$$
$$\Sigma\frac{f_k}{(3x_k)^2 H_k^2\cos^2\alpha_k + 30}(E_k + i\theta)$$
$$\doteq 12\pi^{-1/2}\kappa z_0^{1/2}e^{-3\pi i/4 - iz_0\theta}\left(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\right)^{1/2}$$
$$\Sigma C_k e^{2\zeta_1 - i\nu_k\theta}(E_k + i\theta)$$

where

$$C_k = \left[\frac{\left(1+\frac{\nu}{z_0}\right)^{3/2} M_1}{(3x)^2 H^2\cos^2\alpha + 30}\cdot\frac{w_1}{\overline{w}_1}e^{\pi i/2 - 2\zeta_1}\right]_{\nu=\nu_k}$$

is independent of θ.

If $$\psi_0 = -i\kappa\cos^2\tfrac{1}{2}\theta\,.\,e^{-2iz_0\sin\frac{1}{2}\theta}$$

is the value of ψ at the same point due to the same oscillator in free space,

$$\frac{\psi_{01}}{\psi_0} = 12\pi^{-1/2}\,.\,z_0^{1/2}e^{-\pi i/4 - iz_0(\theta - 2\sin\frac{1}{2}\theta)}\left(\sin\frac{\theta}{2}\right)^{1/2}\left(\cos\frac{\theta}{2}\right)^{-3/2}$$
$$\sum_{k=0} C_k e^{2\zeta_1 - i\nu_k\theta}(E_k + i\theta).$$

Calculation of C_k *and* E_k.

The values of $x_0, x_1, x_2\ldots$, the zeros of $K_{2/3}(xe^{-3\pi i/2})$, are

$$x_0 = \cdot 6854, \quad x_1 = 3\cdot 902, \quad x_2 = 7\cdot 05, \quad x_3 = 10\cdot 20,$$
$$x_4 = 13\cdot 34, \quad x_5 = 16\cdot 49\ldots.$$

* *Cf.* Watson's 'Bessel Functions,' chap. iii.

The quantities H and α are tabulated in Watson's 'Bessel Functions' for values of x up to 16; thereafter at a root $x=x_k$.

$$H=\sqrt{\frac{2}{\pi x}} \quad \text{and} \quad \alpha=150^\circ.$$

Also

$$2\nu_k=(3x_k)^{2/3}z_0^{1/3}e^{-\pi i/3}, \qquad (3\zeta_1)^{2/3}=2z_1^{-1/3}(\nu-z_1+z_0), \quad (1)$$

$$\frac{w_1}{\bar{w}_1}=\frac{K_{1/3}(\zeta_1 e^{-\pi i})}{K_{1/3}(\bar{\zeta}_1 e^{\pi i})}=\frac{\zeta_1^{-1/2}e^{\pi i/2+\zeta_1}\left\{1+\frac{5}{72\zeta_1}+\frac{5\,77}{2.72^2\zeta_1^2}\cdots\right\}}{\bar{\zeta}_1^{-1/2}e^{-\pi i/2+\bar{\zeta}_1}\left\{1+\frac{5}{72\bar{\zeta}_1}+\frac{5.77}{2.72^2\bar{\zeta}_1^2}\cdots\right\}},$$

if $|\zeta_1|$ is not too small*, and this, after simplification becomes $\frac{w_1}{\bar{w}_1}=e^{2\zeta_1-\pi i/2}\left\{1+\frac{5}{36\zeta_1}+\frac{50}{72^2\zeta_1^2}\cdots\right\}$.

Further,

$$M_1=-\frac{\rho\frac{w_{11}'}{w_{11}}-\frac{w_1'}{w_1}}{\rho\frac{w_{11}'}{w_{11}}-\frac{\bar{w}_1'}{\bar{w}_1}},$$

and the two quantities in the numerator are nearly equal, so that a fairly accurate determination of $\frac{w_{11}'}{w_{11}}$ and $\frac{w_1'}{w_1}$ is required. For the smallest values of k the asymptotic expansions of the Bessel functions are not sufficiently accurate, and the ascending series have to be used; but when k is greater than one the asymptotic series have been found to be adequate. If w is the same function of ζ as w_1 is of ζ_1 and w_{11} of ζ_{11}, the asymptotic series is given by

$$-\frac{w'}{w}=3^{1/3}z^{-1/3}\zeta^{1/3}\frac{K_{2/3}(\zeta e^{-\pi i})}{K_{1/3}(\zeta e^{-\pi i})}$$

$$=\left(\frac{3\zeta}{z}\right)^{1/3}\frac{1-\frac{7}{72\zeta}-\frac{7.65}{2.72^2\zeta^2}-\frac{7.65.209}{6.72^3\zeta^3}\cdots}{1+\frac{5}{72\zeta}+\frac{5.77}{2.72^2\zeta^2}+\frac{5.77.221}{6.72^3\zeta^3}\cdots}$$

$$=\left(\frac{3\zeta_1}{z_1}\right)^{1/3}\left\{1-\frac{1}{6\zeta}-\frac{5}{72\zeta^2}-\frac{5}{72\zeta^3}\cdots\right\}$$

on expanding.

* For the asymptotic expansions employed see Watson's 'Bessel Functions,' chap. vii.

At the first two poles ($k=0$ and $k=1$), $K_{2/3}(\zeta e^{-\pi i})$ and $K_{1/3}(\zeta e^{-\pi i})$ must be expressed in terms of $I_{\pm 2/3}(\zeta e^{-\pi i})$ and $I_{\pm 1/3}(\zeta e^{-\pi i})$, and hence as series of ascending powers of ζ. Hence

$$C_k = \left[\frac{\left(1+\frac{\nu}{z_0}\right)^{3/2} M_1}{(3x)^2 H^2 \cos^2\alpha + 30^c} \frac{w_1}{\bar{w}_1} e^{\pi i/2 - 2\zeta_1} \right]_{\nu=\nu_k}$$

can be calculated without any great difficulty, ν_k and ζ_1 being determined by the above expressions (1).

In order to find E_k it is necessary to calculate $\frac{1}{M_1}\frac{\partial M_1}{\partial \nu}$ and $\frac{\bar{w}_1}{w_1}\frac{\partial}{\partial \nu}\frac{w_1}{\bar{w}_1}$; the former is the most laborious part of the whole calculation, as it depends on the difference of quantities which are nearly equal, and requires very great accuracy in the early stages of the arithmetic to ensure a small error in the result.

$\frac{\partial}{\partial \nu}\frac{w_1}{\bar{w}_1}$ is readily found from the asymptotic series already given for $\frac{w_1}{\bar{w}_1}$, viz.,

$$e^{2\zeta_1 - \pi i/2}\left\{1+\frac{5}{36\zeta_1}+\frac{50}{72^2\zeta_1^2}\cdots\right\},$$

and so

$$\frac{\bar{w}_1}{w_1}\frac{\partial}{\partial \nu}\frac{w_1}{\bar{w}_1} = \frac{\partial \zeta_1}{\partial \nu}\left\{2-\frac{5}{36\zeta_1^2}\cdots\right\}$$

$$= 2\left(\frac{3\zeta_1}{z_1}\right)^{1/3}\left\{1-\frac{5}{72\zeta_1^2}\cdots\right\},$$

since $$(3\zeta_1)^{2/3} = 2.z_1^{-1/3}.(\nu - z_1 + z_0).$$

The term $\frac{5}{72\zeta_1^2}$ is negligible in the calculations below except at the first pole ($k=0$), where it has a small effect.

To find $\frac{1}{M_1}\frac{\partial M_1}{\partial \nu}$, let

$$N = \rho\frac{w_{11}'}{w_{11}} - \frac{w_1'}{w_1} \quad \text{and} \quad D = \rho\frac{w_{11}'}{w_{11}} - \frac{\bar{w}_1'}{\bar{w}_1},$$

so that

$$M_1 = -\frac{N}{D} \quad \text{and} \quad \frac{1}{M_1}\frac{\partial M_1}{\partial \nu} = \frac{1}{N}\frac{\partial N}{\partial \nu} - \frac{1}{D}\frac{\partial D}{\partial \nu}.$$

Now if $|\zeta|$ is not too small,

$$\frac{w'}{w} = -\left(\frac{3\zeta}{z}\right)^{1/3}\left\{1-\frac{1}{6\zeta}-\frac{5}{72\zeta^2}-\frac{5}{72\zeta^3}\cdots\right\},$$

so that

$$\frac{\partial}{\partial\nu}\frac{w'}{w}=-\left(\frac{1}{3z^2\zeta}\right)^{1/3}\left\{1+\frac{1}{3\zeta}+\frac{25}{72\zeta^2}+\frac{5}{9\zeta^3}\cdots\right\},$$

where, as usual with such series, the best approximation is obtained by stopping at the term next before the smallest.

In the example given below the values of $\frac{1}{\mathrm{N}}\frac{\partial \mathrm{N}}{\partial\nu}$ and $\frac{1}{\mathrm{D}}\frac{\partial \mathrm{D}}{\partial\nu}$ calculated from these asymptotic series are adequate, unless at the first two poles ($k=0$ and $k=1$); in these cases $\frac{\mathrm{K}_{2/3}(\zeta e^{-\pi i})}{\mathrm{K}_{1/3}(\zeta e^{-\pi i})}$ must be calculated from the ascending series, and $\frac{\partial}{\partial\nu}\frac{w'}{w}$ can then be deduced as follows.

Since

$$\frac{\partial}{\partial z}z^{2/3}\mathrm{K}_{2/3}(z)=-z^{2/3}\mathrm{K}_{1/3}(z),$$

$$\frac{\partial}{\partial\zeta}\zeta^{2/3}\mathrm{K}_{2/3}(\zeta e^{-\pi i})=\zeta^{2/3}\mathrm{K}_{1/3}(\zeta e^{-\pi i}),$$

and therefore

$$\frac{\partial}{\partial\zeta}\frac{\zeta^{2/3}\mathrm{K}_{2/3}(\zeta e^{-\pi i})}{\zeta^{1/3}\mathrm{K}_{1/3}(\zeta e^{-\pi i})}=\frac{\zeta\mathrm{K}^2_{1/3}(\zeta e^{-\pi i})-\zeta\mathrm{K}^2_{2/3}(\zeta e^{-\pi i})}{\zeta^{2/3}\mathrm{K}^2_{1/3}(\zeta e^{-\pi i})}$$

$$=\zeta^{1/3}\left\{1-\frac{\mathrm{K}^2_{2/3}(\zeta e^{-\pi i})}{\mathrm{K}^2_{1/3}(\zeta e^{-\pi i})}\right\}.$$

Hence

$$\frac{\partial}{\partial\nu}\frac{w'}{w}=-\left(\frac{3\zeta}{z}\right)^{2/3}\left\{1-\frac{\mathrm{K}^2_{2/3}(\zeta e^{-\pi i})}{\mathrm{K}^2_{1/3}(\zeta e^{-\pi i})}\right\},$$

and

$$\frac{\partial \mathrm{N}}{\partial\nu}=\left(\frac{3\zeta_1}{z_1}\right)^{2/3}\left\{1-\frac{\mathrm{K}^2_{2/3}(\zeta_1 e^{-\pi i})}{\mathrm{K}^2_{1/3}(\zeta_1 e^{-\pi i})}\right\}$$

$$-\rho\left(\frac{3\zeta_{11}}{z_{11}}\right)^{2/3}\left\{1-\frac{\mathrm{K}^2_{2/3}(\zeta_{11}e^{-\pi i})}{\mathrm{K}^2_{1,3}(\zeta_{11}e^{-\pi i})}\right\}$$

$$\frac{\partial \mathrm{D}}{\partial\nu}=\left(\frac{3\zeta_1}{z_1}\right)^{2/3}\left\{1-\frac{\mathrm{K}^2_{2/3}(\zeta_1 e^{+\pi i})}{\mathrm{K}^2_{1/3}(\zeta_1 e^{+\pi i})}\right\}$$

$$-\rho\left(\frac{3\zeta_{11}}{z_{11}}\right)^{2/3}\left\{1-\frac{\mathrm{K}^2_{2/3}(\zeta_{11}e^{-\pi i})}{\mathrm{K}^2_{1/3}(\zeta_{11}e^{-\pi i})}\right\}.$$

In the case tabulated below $|\zeta_1|=3{\cdot}9004$ and $|\zeta_{11}|=3{\cdot}2180$ at the second pole, and the values found for $\frac{\partial}{\partial\nu}\cdot\frac{w_1'}{w_1}$ are

·001456 + ·002555 i from the asymptotic series, and ·001436 + ·002600 i from the ascending series; the corresponding values of $\frac{1}{M_1}\frac{\partial M_1}{\partial \nu}$ (w_{11}'/w_{11} being calculated from the ascending series) are ·0191 − ·0437 i and ·0185 − ·0447 i, and E_k is found to be ·169 − ·233 i from the first and ·169 − ·232 i from the second and more accurate value.

The following values of C_k, E_k, ζ_{1k}, and ν_k have been calculated for the case when r_0 = radius of the earth = 6367·4 km., r_1 = 6467·4 km. (*i. e.*, the height of the reflecting surface above the surface of the earth is 100 km.), λ = 18,750 m., K'/K = ·99, and when the earth is supposed perfectly conducting. The values given are believed to be sufficiently accurate to give $\left|\frac{\psi_{01}}{\psi_0}\right|$ correct to the second decimal place for values of θ greater than 10°.

	$k=0$.	$k=1$.	$k=2$.
$\lvert C_k \rvert$.	·0325	·00475	·00171
arg C_k.	−12° 8′	−75°	−93° 58′
E_k.	·0570 − ·2394 i	·169 − ·232 i	·262 − ·268 i
$2\zeta_{1k}$.	2·93 − 5·87 i	7·80 − ·10 i	10·35 + 5·34 i
$i\nu_k$.	9·014 + 5·204 i	28·73 + 16·59 i	42·63 + 24·61 i

	$k=3$.	$k=4$.	$k=5$.
$\lvert C_k \rvert$.	·00092	·000582	·000406
arg C_k.	−102° 21′	−108° 24′	−111° 43′
E_k.	·320 − ·291 i	·367 − ·309 i	·405 − ·326 i
$2\zeta_{1k}$.	12·18 + 10·90 i	13·62 + 16·50 i	14·89 + 22·22 i
$i\nu_k$.	54·54 + 31·49 i	65·22 + 37·66 i	75·12 + 43·37 i

These values being known, $\frac{\psi_{01}}{\psi_0}$ is given by the formula

$$\frac{\psi_{01}}{\psi_0} = 12\pi^{-1/2} z_0^{1/2} \left(\sin\frac{\theta}{2}\right)^{1/2} \left(\cos\frac{\theta}{2}\right)^{-3/2} e^{-\pi i/4 - i z_0(\theta - 2\sin\theta/2)} . \mathrm{S},$$

where

$$\mathrm{S} = \sum_{k=0}^{k=\infty} \mathrm{C}_k e^{2\zeta_1 k - i\nu_k \theta} (\mathrm{E}_k + i\theta) = \sum_k u_k .$$

When $\theta = 10°$,

$$u_5 = \cdot 0010 - \cdot 0002\, i \quad \text{and} \quad \sum_{k=0}^{k=5} u_k = \cdot 0009 - \cdot 0032\, i ;$$

when $\theta = 11°$ or more the contribution of u_5 to S is almost negligible. The value for S got from the first six poles may therefore be slightly in error when $\theta = 10°$, and in order to get it accurately the constants for the next pole $k = 6$ would have to be calculated; but when $\theta > 10°$, the constants given are sufficient. When $\theta > 20°$, the whole of the effective part of S is contributed by the first pole, and the arithmetic is comparatively light. The values found for $\frac{\psi_{01}}{\psi_0}$ are :—

θ.	10°.	11°.	12°.	13°.	14°.	15°.	16°.
$\left\|\frac{\psi_{01}}{\psi_0}\right\|$.	·31 (?)	·33	·36	·38	·40	·41	·43
$\arg\left\|\frac{\psi_{01}}{\psi_0}\right\|$.	−146° 19′	−141° 29′	−141° 15′	−146° 6′	−153° 4′	−167° 55′	+176° 15′

θ.	17°.	18°.	19°.	20°.	22°.	25°.
$\left\|\frac{\psi_{01}}{\psi_0}\right\|$.	·45	·45	·45	·44	·42	·37
$\arg\left\|\frac{\psi_{01}}{\psi_0}\right\|$.	+154° 54′	+130° 52′	113° 14′	69° 53′	−7° 5′	−151° 16′

The values of $\frac{\psi_{01}}{\psi_0}$ from $\theta=3°$ to $\theta=7°$ have been calculated from Macdonald's solution, corrected when necessary by the addition of terms got by including second approximations; these, and the values of $\frac{\psi_{00}}{\psi_0}$ for the diffracted wave, obtained from the formula given in the beginning of this paper, are tabulated below, along with the value of $\left|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right|$ found from them, this being the intensity of the measured signal when only one reflected wave is present. The values of $\left|\frac{\psi_{00}}{\psi_0}\right|$ are added for comparison.

θ.	3°.	3° 20′.	3° 40′.	4°.	4° 20′.	4° 40′.	5°.
$\frac{\psi_{01}}{\psi_0}$.	0·01 −0·01 i	0·01 +0·02 i	−0·02 +0·02 i	−0·03 −0·01 i	−0·02 −0·04 i	0·02 −0·05 i	0·05 −0·03
$\frac{\psi_{00}}{\psi_0}$.	1·76 −0·23 i	1·71 −0·27 i	1·66 −0·31 i	1·62 −0·35 i	1·57 −0·39 i	1·51 −0·43 i	1·46 −0·47 i
$\left\|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right\|$.	1·79	1·74	1·67	1·63	1·61	1·60	1·59
$\left\|\frac{\psi_{00}}{\psi_0}\right\|$.	1·77	1·73	1·69	1·66	1·62	1·57	1·54

θ.	5° 20′.	5° 40′.	6°.	6° 20′.	6° 40′.	7°.
$\frac{\psi_{01}}{\psi_0}$.	0·07 +0·00 i	0·07 +0·04 i	0·04 +0·08 i	0·02 +0·10 i	−0·02 +0·10 i	−0·07 +0·10 i
$\frac{\psi_{00}}{\psi_0}$.	1·40 −0·51 i	1·35 −0·55 i	1·29 −0·59 i	1·22 −0·62 i	1·16 −0·66 i	1·09 −0·69 i
$\left\|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right\|$.	1·56	1·51	1·42	1·35	1·27	1·18
$\left\|\frac{\psi_{00}}{\psi_0}\right\|$.	1·50	1·46	1·42	1·37	1·34	1·29

Values of $\frac{\psi_{01}}{\psi_0}$ for $\theta > 10°$ have already been given. The corresponding values of $\left|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right|$ and $\left|\frac{\psi_{00}}{\psi_0}\right|$ are as follows :—

θ.	10°.	11°.	12°.	13°.	14°.	15°.	16°.
$\left\|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right\|$.	1·05(?)	1·03	1·06	1·03	0·99	0·95	0·91
$\left\|\frac{\psi_{00}}{\psi_0}\right\|$.	0·96	0·87	0·77	0·69	0·61	0·54	0·48
θ.	17°.	18°.	19°.	20°.	22°.	25	
$\left\|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right\|$.	0·88	0·81	0·76	0·73	0·64	0·23	
$\left\|\frac{\psi_{00}}{\psi_0}\right\|$.	0·42	0·37	0·33	0·29	0·22	0·15	

The values of $\left|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right|$ at 7° and 10° may be in error by a unit in the second decimal place; it is believed that the others are correct. The graph of $\left|\frac{\psi_{00}+\psi_{01}}{\psi_0}\right|$ suggests that between $\theta = 7°$ and $\theta = 10°$ the signal intensity falls to a minimum between 8° and 9°, and then rises to the value 1·06 at 10°, but it would be advantageous to obtain values at these intermediate distances by some other method.

I have to acknowledge my indebtedness to Prof. H. M. Macdonald for much help and encouragement in the preparation of this paper.

II. *The Fingering of Wind Instruments.* *By* Eric J. Irons, *Ph.D.* *

1. *Introductory.*

In 1924 Paris [1] derived a formula for the free periods of a stopped pipe having two Helmholtz resonators on the side, and it may be noted that if in his equation (26) we make the volumes of the resonators infinite by putting $n_s=0$, we obtain an expression for the resonant frequencies of a stopped pipe having two side holes.

More recently Richardson [2], guided by impedance principles, has discussed the theory of fingering on the wood-wind, and has made some measurements on flutes and clarinets. Basing his argument upon the approximation (due to Steinhausen [3]) that when two side holes are open the instrument may be considered as one pipe extending from the mouth to the first hole and another pipe extending from this hole to the second hole (at which an antinode is supposed to form), Richardson has, in effect, considered the system as a shortened pipe with only one hole open at a time.

The theory of the present paper renders possible the calculation of the pitch of the note emitted by an instrument when any number of side holes are open.

2. *Theoretical.*

In a former paper [4] a simple proof was given of Webster's [5] formula

$$Z_1 = \beta/\sigma \cdot \frac{Z_2 \cos kl - (\beta/\sigma)\sin kl}{Z_2 \sin kl + (\beta/\sigma)\cos kl} \quad . \quad . \quad . \quad (1)$$

for the impedance, Z_1, at one end of a tube of length l † and area of cross-section σ in terms of the impedance, Z_2, at the other end, and β the product of the elasticity of the gas and k ($=2\pi n/a$ in the usual notation).

For the purposes of calculation it is convenient to write (1) in the form

$$Z_1 = \frac{Z_2 - (\beta/\sigma)\tan kl}{1 + (\sigma/\beta) Z_2 \tan kl} \quad . \quad . \quad . \quad . \quad . \quad (1.1)$$

* Communicated by the Author.

† It is to be understood throughout the paper that the length of a column of gas is its geometrical length together with any appropriate end-correction or corrections.

If, now, we suppose the impedance Z_2 at $x=l$ to be zero. and that l is so small that kl may be written for $\tan kl$, it follows that

$$Z_1' = -(\beta/\sigma)kl = -\beta k/c, \quad . \quad . \quad . \quad . \quad (2)$$

where c is the conductance of the resulting short channel or orifice.

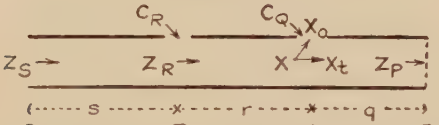
Next consider the system shown in fig. 1. The impedance at Q due to the air in the tube of length q is, by (1.1), equal to

$$\frac{Z_P - (\beta/\sigma)\tan kq}{1+(\sigma/\beta)Z_P \tan kq} = M \text{ (say)}.$$

The impedance of the orifice at Q is, by (2), equal to

$$-\beta k/c_Q = N \text{ (say)}.$$

Fig. 1.



Following the principle enunciated by Rayleigh [6] we shall assume the air in the neighbourhood of Q to be incompressible, so that a volume displacement X arriving at Q will give rise to volume displacements X_0 and X_t through the orifice and down the tube QP respectively, such that $X = X_0 + X_t$. Since at any instant the excess pressure p_Q on the incompressible volume of gas near Q is constant throughout that volume, $X/p_Q = X_0/p_Q + X_t/p_Q$, or, with Webster's notation, where impedance is defined as the ratio p/X, $1/Z_Q = 1/N + 1/M$, which determines Z_Q.

Z_R may be shown in an exactly similar manner to be given by

$$1/Z_R = \frac{1+(\sigma/\beta)Z_Q \tan kr}{Z_Q - (\beta/\sigma)\tan kr} - c_R/\beta k.$$

Finally, the impedance at S is given by

$$Z_S = \frac{Z_R - (\beta/\sigma)\tan ks}{1+(\sigma/\beta)Z_R \tan ks}.$$

If the tube is resounding to a source at S (the source being such as to make S an antinode) *, it follows that a very small

* As, for example, in an organ pipe or flute. For an instrument of the clarinet type S is a node and for resonance $Z_S = \infty$.

excess pressure p_s will give rise to a very large volume displacement X_s, so that $Z_s = p_s/X_s = 0$, in the absence of friction. From a knowledge of the dimensions of the system, it follows that the resonant frequency may be calculated by the method of successive approximations. Furthermore, the method is applicable to any number of side holes *.

When only one side hole is open the problem lends itself to graphical treatment in a similar manner to Paris's formula [1] for a stopped pipe having one Helmholtz resonator on the side.

Disregarding c_R (fig. 1) and equating Z_R to zero gives $Z_Q - (\beta/\sigma)\tan kr = 0$ or, substituting the value of Z_Q,

$$(\sigma/\beta)\cot kr = -c_Q/\beta k + \frac{1 + (\sigma/\beta)Z_P \tan kq}{Z_P - (\beta/\sigma)\tan kq}.$$

If the tube is open at P, $Z_P = 0$ and

$$-1/(\cot kr + \cot kq) = k\sigma/c_Q \; ; \quad . \; . \; . \quad (3)$$

or, if it is closed, $Z_P = \infty$ and

$$-1/(\cot kr - \tan kq) = k\sigma/c_Q. \; . \; . \; . \; . \quad (4)$$

Let the frequency of the pipe, when no side holes are open, be n_0 and define a variable f such that $f = r/(r+q)$, when (3) and (4) will become

$$\frac{-1}{\cot\pi \cdot \frac{n}{n_0} \cdot f + \cot\pi \cdot \frac{n}{n_0} \cdot (1-f)} = \frac{\pi}{L} \cdot \frac{n}{n_0} \cdot \frac{\sigma}{c} \; . \; . \; . \; . \quad (3.1)$$

and

$$\frac{-1}{\cot\frac{\pi}{2} \cdot \frac{n}{n_0} \cdot f - \tan\frac{\pi}{2} \cdot \frac{n}{n_0} \cdot (1-f)} = \frac{\pi}{2L} \cdot \frac{n}{n_0} \cdot \frac{\sigma}{c}, \quad . \; . \quad (4.1)$$

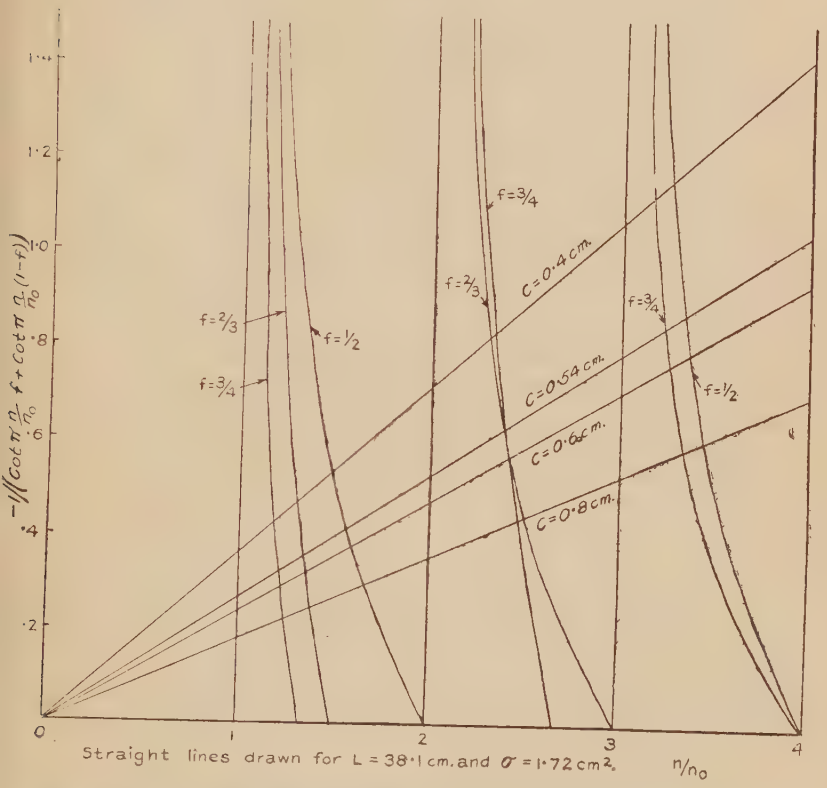
where L is the total length of the pipe and the subscript of c is dropped.

Plotting values of the left-hand sides of (3.1) and (4.1) against n/n_0 for various values of f gives rise to the curves

* The method of taking the impedances of an open and a closed pipe as $-(\beta/\sigma)\tan kl$ and $+(\beta/\sigma)\cot kl$ respectively (where impedance is defined by p/X); adding the impedances of the component parts in series (or by a "parallel" rule for side holes); and equating to zero for resonance is, as the results of the present paragraph show, applicable in general only where the number of tubes does not exceed two [4 & 7]. See also Hanson [8]. Richardson's theory [2] as it stands cannot therefore be extended to include more than the one side hole which he has treated.

of figs. 2 and 3 respectively; and plotting values of the right-hand sides for *a given hole in a given instrument* against n/n_0 gives rise to the series of straight lines in the same figures. The intersections of the curves and the straight lines determine the resonant frequencies in terms of n_0. It is to be noted that the curves—as distinct from

Fig. 2.

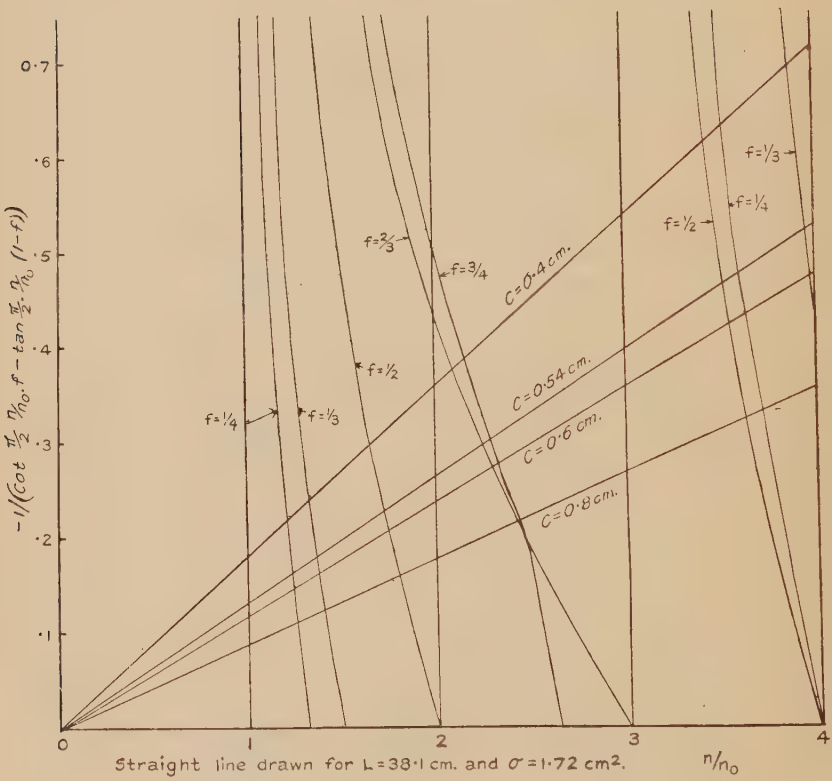


the straight lines—will serve for any instrument for which the value of n_0 is known.

Equation (4.1) and fig. 3 are here given to explain experiments with an instrument having an "antinodal" mouth and stopped end. The same equation and diagram will serve to illustrate the properties of instruments of the clarinet type having a "nodal" (reed) mouth and open end if, in terms of fig. 1, f is redefined as equal to $q/(r+q)$.

It is of theoretical interest to note from figs. 2 and 3 the values of the frequencies indicated for the instances in which c is very large (equivalent to nearly opening the tube) and very small (equivalent to practically no side opening), and to compare these values with those derived from the corresponding "stationary wave-diagrams" for the pipe.

Fig. 3.



It would appear that when c is large the longer portion of the tube governs the frequency; this is to be expected as, *ceteris paribus*, energy is proportional to the square of the frequency, and therefore inversely proportional to the square of the length.

3. *Practical.*

The preceding theory has been used to calculate the notes emitted by a flageolet having various holes open, but before

describing the results obtained it will be necessary to refer to a

Preliminary Investigation.

The end correction at the end of an unflanged cylindrical pipe is well known to approximate to 0·6 times the radius of the pipe [9], but the mouth correction is a more indefinite quantity and does not appear to have received the attention it deserves. To obtain a value for the mouth correction of the instrument to be used and to trace its variation (if any) with frequency, an auxiliary mouth-piece, of similar structure to that of the flageolet, was made to excite various lengths of closed and open tube into resonance. We have for a closed pipe, $L=a/4n-C$ (where L, C, a, and n represent tube-length, mouth correction, velocity of sound, and frequency respectively), and for an open pipe, $L=a/2n-C$, where L now represents the geometrical length of the pipe together with 0·6 times its radius. Plots of L against $1/n$ (fig. 4) are sensibly rectilinear, from which it follows that, to within the limits of the present experimental error (n being determined by a sonometer), C is constant. Fig. 4 also shows that the correction is approximately the same whether the tube is open or closed, and is equal to 2·1 cm., which is 2·8 times the tube radius *. A careful comparison of the frequencies obtained when the actual flageolet was sounded (with its side holes closed), firstly when open and secondly when closed by a tightly-fitting brass stop protruding 0·3 cm. into the tube, also yielded a value of the mouth correction equal to 2·1 cm., which value was accordingly adopted in the calculations which follow. This measurement is a delicate one, a slight error in one of the pitches involved making a considerable difference in the value of the mouth correction.

The mean of the three values of a determined from fig. 4

* The following calculation serves to show that this correction is of the right order. It has been stated by Cavaillé-Coll [10] that the total of the mouth and the open end corrections for a square pipe is twice the distance (b) from the side containing the lip to the back of the pipe. The radius of the circle having the same area as the cross-section of the pipe is given by $b^2=\pi r^2$, so that the total of the corrections for a cylindrical pipe should be about $2b=2\sqrt{\pi}\,.\,r=3{\cdot}5\,.\,r$, which compares favourably with the $(2{\cdot}8+{\cdot}6)\,.\,r$ above.

A similar result has been obtained for the mouth correction of a cylindrical organ pipe (see forthcoming paper on Constrictions in Organ Pipes).

and the above experiment was 350 metres/sec., which is reasonable figure having regard to temperature effects*.

Fig. 4.

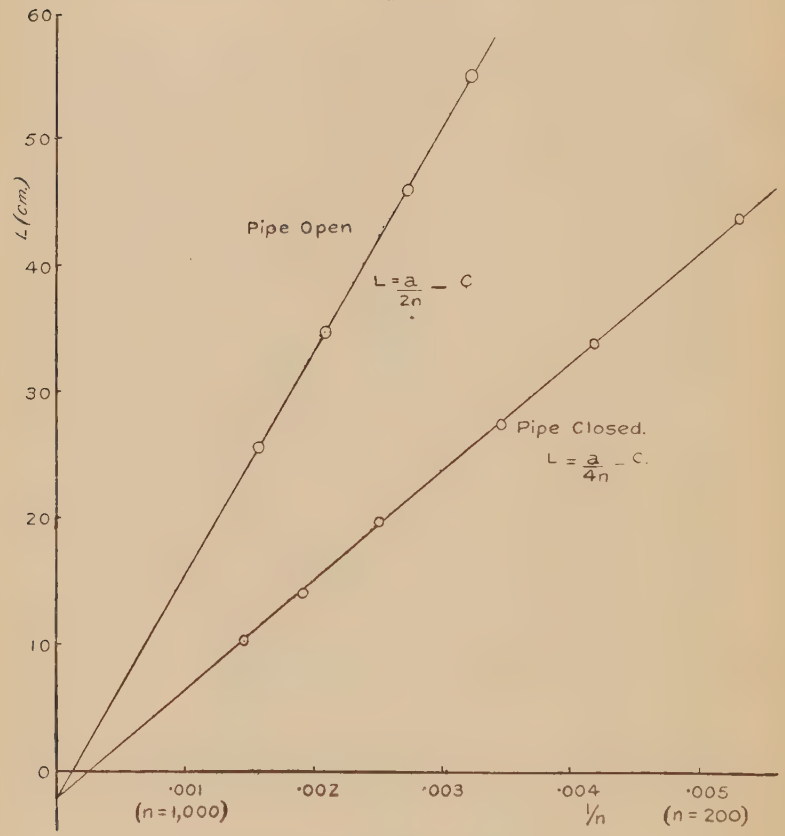
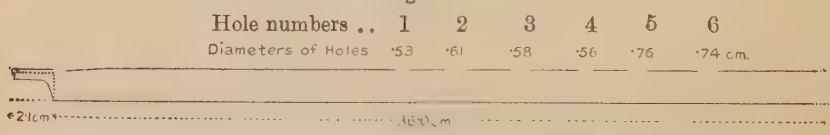


Fig. 5.



Investigation of Tones emitted by Flageolet.

Fig. 5 is a scale drawing of the flageolet, and, following Mason's [11] procedure (derived from theoretical reasoning in

* The air in an instrument is partly expired air, and the chief difference between this and inspired air is that 5 per cent. of the oxygen by volume in inspired air is replaced by CO_2.

connexion with acoustical filters), the lengths of the constituent air-columns were measured from opposite the centres of the side holes.

We shall, for lack of more precise data, follow Rayleigh and take the conductance of an orifice in a thin wall as equal to its diameter, although it has been found that for smaller wave-lengths and somewhat larger holes in a cap closing a tube the conductances exceed this value [7], [12].

The note emitted by the instrument depends on the blowing pressure, and the values tabulated below (Table I.) are for the normal frequencies, *i. e.*, those frequencies which are compatible with the formulæ $a=4n\mathrm{L}$ and $a=2n\mathrm{L}$ for a closed and an open pipe respectively. The theoretical values were obtained by successive approximations using four-figure tables.

TABLE I.

Frequencies of Notes emitted by Flageolet.

Side holes open (fig. 5).	Open pipe ($Z_P=0$, fig. 1).		Closed pipe ($Z_P=\infty$, fig. 1).		F_1.	F_2.
	Obs.	Cal.	Obs.	Cal.		
1	913	920	830	827	946	
123456	861	855	862	855	946	876
23456	769	763	770	763	829	777
2	724	712	766	762	829	
3456	691	679	690	679	732	688
3	664	652	708	708	732	
456	618	608	598	608	648	617
4	594	590	537	541	648	
56	567	565	554	563	595	570
5	563	560	534	545	595	
6	507	509	489	498	538	

Investigation with Auxiliary Whistle.

To investigate more fully the notes emitted when only one side hole is open, the auxiliary mouth-piece already mentioned was fitted with a tube of the same cross-section and length as the flageolet. A shorter tube, of length equal to the open end correction of the first tube, terminating in a solid cap, was used to close the first tube when desired; in this manner the "length" of the tube was unaltered. Side holes of diameter equal to 0·54 cm. were bored in the

tube at distances equal to $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, and $\frac{3}{4}$ of its corrected length from the ("corrected") mouth end. The lower notes emitted under different blowing pressures when each side hole was open in turn are tabulated in Table II. (in terms of the fundamental frequencies of the tube n_0) for the instances in which the tube was open and closed by the cap.

Straight-line plots of the right-hand sides of equations (3.1) and (4.1) for $c=0{\cdot}54$ cm. and $L=38{\cdot}1$ cm. were made on figs. 2 and 3, and the theoretical values of n/n_0 were read off. From the symmetry of equation (3.1) it will be seen that the same notes should be emitted when $f=\frac{1}{4}$ or $\frac{3}{4}$, or when $f=\frac{1}{3}$ or $\frac{2}{3}$.

TABLE II.

Frequencies of Notes emitted by Auxiliary Whistle.
(Given as the ratio of the frequency of the note to that of the fundamental of the pipe with no side holes open.)

f.	Open pipe.		Closed pipe.	
	Obs.	Cal.	Obs.	Cal.
$\frac{1}{4}$	1·20*	1·22	1·24*	1·22
	2·37	2·39	3·61	3·60
	3·18	3·22		
$\frac{1}{3}$	*	1·35	1·34*	1·36
	2·33	2·38	3·83	3·96
$\frac{1}{2}$	1·54	1·57	1·76	1·73
	3·17	3·32	3·62	3·52
$\frac{2}{3}$	1·38	1·35	2·20	2·24
	2·35	2·38		
$\frac{3}{4}$	1·23	1·22		
	2·37	2·39	2·21	2·28
	3·16	3·22		

* Obtained with difficulty.

4. *Discussion of Results obtained with* :

A. *The Flageolet.*

As an approximation let us first suppose that the note emitted by an instrument is governed solely by the distance between the mouth and the first open hole, and that this distance represents half a wave-length. Frequencies calculated on this assumption are tabulated under F_1 in Table I., and although they follow the general trend of the results it will be noted that the approximation is not a good one.

As a nearer approximation let us, in those instances in which more than one hole is open, follow Richardson [2], and consider the resonance system to consist of two pipes with one side hole (*cf.* § 1); the results then obtained are tabulated under F_2 (Table I.), and compare very favourably with the observed values—especially where the "ventilation" at the end of the flageolet remote from the mouth is good. It would, in fact, appear that there is little, if anything, to be gained by considering the impedance beyond the second open hole, so that equation (3), having due regard to the interpretation of L, represents very nearly the behaviour of the flageolet. In consequence, figs. 2 and 3 assume a new importance as summarizing in a graphical manner all that we require to know concerning the tones such an instrument emits.

B. *Auxiliary Whistle.*

A certain amount of difficulty was experienced in determining the results recorded in Table II., inasmuch as the blowing pressure had to be regulated to a nicety, the mouth-piece did not receive expert voicing, and the tones proper to the pipe with a side hole open were liable to be masked by the overtones to be expected if there had been no side hole—the presence of a hole at an antinode facilitating the production of these overtones. Special difficulty was experienced in obtaining the lowest notes when the side hole was near the mouth. Taken altogether the results appear to indicate that the theory is capable of predicting the frequencies of overtones as far as tested (*i. e.*, up to $n/n_0=4$), and shows that they are not, in general, harmonic.

As a final application of our graphical solution let us follow Richardson and consider how a given note may be flattened by fingering and cross-fingering.

We will suppose that on a given instrument we have holes, the distances between which are as represented in fig. 6, and that we require to flatten very slightly the note obtained by playing the instrument as in *1*. This may be done by :—

(1) Partially covering hole A (fingering) and thus reducing its conductance, which, in terms of fig. 3, means that the gradient of the straight line for that hole is increased, so that n/n_0 is decreased.

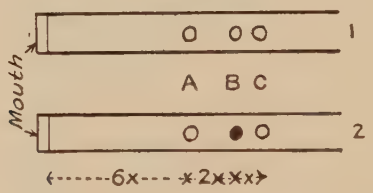
(2) Covering hole B as in fig. 6, *2* (cross-fingering). Before we cover B, $f=\frac{3}{4}$, $L=8x$, and $n_0=a/16x$; after we cover B,

$f=\frac{8}{3}$, L$=9x$, and $n_0=a/18x$. Let us suppose that the conductance of hole A is 0·54 cm., so that the effect of the alteration of L on the straight line (fig. 2) is the same as increasing the value of c to about 0·61 cm. (*vide* equation (3.1)). From fig. 2 we find that the frequency before B is covered is $1{\cdot}22a/16x$, and after it is covered it is $1\ 36a/18x$, so that covering B flattens the note in the ratio $(1{\cdot}36/18)\div(1{\cdot}22/16)$, *i. e.*, by about 1 per cent. of the frequency. In general the reduction would be greater, but this example is convenient as regards explanation in terms of fig. 3.

5. *Conclusion.*

The observations indicate that the "impedance theory" is capable of predicting the frequencies of the tones emitted by the flageolet to within one or two per cent., and to

Fig. 6.



indicate the trend of the results obtained with the auxiliary whistle. The impedance of a conical horn being known [4], it is possible to extend the argument to instruments having that form, and, in fact, it is to be expected that the theory may lead to the better understanding of a number of musical instruments.

In conclusion, I wish to thank Prof. C. H. Lees and Dr. E. G. Richardson for their interest in this paper, and to express my indebtedness and thanks to Mr. B. C. Fleming-Williams, a senior student, for his able assistance with the frequency measurements.

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III. *The Magnetic and Magneto-thermal Properties of Ferromagnetics.* *By* Edmund C. Stoner, *Ph.D.* (*Cambridge*), *Reader in Physics at the University of Leeds* *.

Introduction.

THE theory of para- and ferromagnetism associated with the names of Langevin and Weiss has been remarkably successful in correlating a wide range of experimental facts. Langevin's treatment applies to a system of molecules whose mutual magnetic interaction can be neglected, and each of which possesses a magnetic moment which can assume any orientation with respect to an applied field. Weiss extended the theory by assuming that the molecules were acted on by a molecular field, NI, proportional to the intensity of magnetization, I, in addition to the external field. This hypothesis leads to an expression for the variation of susceptibility with temperature $\left(\chi = \frac{C}{T-\theta}\right)$, which is found to hold experimentally for many paramagnetics; it indicates the conditions under which spontaneous magnetization will occur, as in ferromagnetics; and it leads to curves for the variation of "quasi-saturation" magnetization with temperature below the Curie point, which agree approximately with those observed. The Weiss theory, however, is formal, for the molecular field is such that it cannot be of magnetic origin, and until recently no satisfactory suggestion was made as to how the effects attributed to it could arise.

The main contribution of the quantum theory, before the advent of the recent quantum mechanics, was in connexion with the calculation of the magnetic moments of the elementary carriers (atoms, ions, or molecules) from the experimental data. Whereas the classical theory indicates that the magnetic moment can assume any orientation with respect to an applied field, the quantum theory indicates that the magnetic moment can only assume certain discrete

* Communicated by Prof. R. Whiddington, F.R.S.

values in the field direction. These values depend on the spectral state of the carrier, and can be determined when this is known. The appropriate modification of the Langevin treatment is readily made, and a considerable amount of theoretical and experimental work has been done on this part of the subject *. Although many interesting points of detail remain unexplained, on the whole it may be said that the agreement between the magnetic moments deduced from susceptibility measurements on paramagnetics, and those deduced from spectroscopic observations, are in very satisfactory agreement.

For normal paramagnetics, such as salts, the nature of the carriers is usually fairly certain. In ferromagnetics, on the other hand, it is not known whether the carriers are electrons, atoms, ions, or groups of these. From the extensive magnetic data, it is reasonable to suppose that a fairly definite decision could be arrived at, but at present different lines of attack on the problem seem to lead to entirely different conclusions. For this reason it seems desirable to derive some of the more important quantum theory formulæ bearing on ferromagnetism, as these are necessary in any discussion of the significance of experimental results. The new mechanics is not here involved, and while there is nothing essentially new in the formulæ, no explicit derivation of some of them seems to have been given.

A fundamental advance in the theory of para- and ferromagnetism has been made by Heisenberg, who has shown that the interchange of electrons in atoms, which is characteristic of quantum mechanics, is capable, under certain conditions, of giving rise to those effects which have been partially correlated by the molecular field hypothesis. Even with the particularly simple model which is taken, the calculations are of considerable complexity, and the final results are only to be regarded as approximate. It is, however, the general nature of the results which is of importance. Here, again, it seems desirable to put these results in a form in which their relation to the experimental data is as clearly shown as possible; or, since experimental results have usually been considered with reference to the Weiss theory, to show the relation between the Heisenberg and Weiss theories.

In this paper, then, various theoretical formulæ for ferromagnetics will be derived, and they will be put in such a form as to facilitate comparison with experiment. The

* For a summary and discussion, see E. C. Stoner, Phil. Mag. viii. p. 250 (1929).

experimental results are briefly considered, and the conclusions that can be drawn from them as to the interpretation of ferromagnetic phenomena are discussed.

The Variation of Magnetization with Temperature above and below the Curie Point.

In deriving expressions for the variation of susceptibility above the Curie point, and for the variation of magnetization below, it will be assumed that the carriers in the ferromagnetic are the same in both ranges, and that they all have the same magnetic moment. (Such modifications as may be necessary can readily be made.) When the carriers are regarded as quantized systems, the magnetic moment μ is equal to $jg\mu_B$, where j is the quantum number giving the total angular momentum in Bohr units, g is the Landé splitting factor (equal to the ratio of the magnetic to the mechanical moment), and μ_B is the Bohr unit magneton. Before giving the quantum treatment, the classical formulæ will be set down, so that corresponding expressions may be easily compared. To avoid confusion, a list of the symbols (other than those well established) used is given :—

μ Magnetic moment of carrier. (For a quantum system $\mu = jg\mu_B$, this being the maximum moment in the field direction.)

$\bar{\mu}$ Mean resolved magnetic moment of carriers.

μ_B Bohr unit magneton.

μ_W Weiss unit magneton ($\mu_B = 4{\cdot}97\ \mu_W$).

M_B, M_W. Bohr and Weiss magneton values per gram molecule ($M_W = 1123{\cdot}5$).

L Number of molecules per gram molecule ($M_B = L\mu_B$; $M_W = L\mu_W$).

I Intensity of magnetization (unit volume).

σ Specific intensity of magnetization (unit mass).

σ_0 Saturation value of σ.

σ_M Saturation moment per gram molecule ($\sigma_M = L\mu$).

H_i Molecular field.

H_e External field.

H Total field.

N Weiss molecular field constant ($H_i = NI$).

p Magnetic moment in Weiss magnetons (calculated classically).

$a = \mu H/kT$.

M Molecular weight.

Classical Theory.

The Langevin expression for the magnetization is

$$\bar{\mu}/\mu = \sigma/\sigma_0 = \coth a - 1/a. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For a small

$$\bar{\mu}/\mu = a/3 - a^3/45. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

For a large

$$\bar{\mu}/\mu = 1 - \frac{1}{a} + 2e^{-2a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

The hypothesis of the molecular field is introduced in a second equation,

$$a = \frac{\mu H}{kT} = \frac{\mu H_e}{kT} + \frac{\mu N I}{kT}$$

$$= \frac{\mu H_e}{kT} + \frac{\mu N}{kT}\frac{\rho L \bar{\mu}}{M}$$

$$= \frac{\mu H_e}{kT} + \frac{\sigma_M{}^2 N \rho}{MRT}\frac{\bar{\mu}}{\mu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Curie Point.—In the absence of an external field ($H_e = 0$) spontaneous magnetization can occur if the slope of the straight line given by (2) is less than the slope of the tangent at the origin of (1),

$$\frac{MRT}{\sigma_M{}^2 N \rho} < \tfrac{1}{3},$$

$$T < \frac{N \rho \sigma_M{}^2}{3MR}.$$

The Curie temperature is therefore given by

$$\theta = \frac{N \rho \sigma_M{}^2}{3MR}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Paramagnetism.—Above the Curie point an expression for the susceptibility may readily be obtained from the above equations; the expression will hold if a is small; the temperature must not be too close to the Curie temperature,

$$\chi_M = \frac{M\sigma}{H_e} = \frac{\sigma_M{}^2/3R}{T - \theta} = \frac{C_M}{T - \theta}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For the Weiss magneton value,

$$p = \frac{\sigma_M}{M_W} = \frac{1}{M_W}\sqrt{3RC_M} = 14{\cdot}07\sqrt{C_M}. \quad . \quad . \quad (5)$$

For a normal paramagnetic obeying the Weiss-Curie law, p is obtained directly from the experimental results, which give χ and θ, for the Curie constant C_M is the product of χ_M and $T-\theta$. Although the Weiss magneton is not a fundamental unit, magneton values p are still frequently used, partly for historical reasons, and partly because the p values are convenient numbers and can be derived simply and uniquely from experimental results. The experimental behaviour of a paramagnetic is summarized by the values of p and θ; the usual procedure in dealing with quantized systems is to calculate the theoretical value of p, and to compare this with that found experimentally.

Ferromagnetism.—Below the Curie point the quasi-saturation magnetization at any temperature may be found by extrapolation to zero field of the magnetization observed in high fields, and by various other methods. The theoretical value of this spontaneous magnetization may be obtained by eliminating a between the equations

$$\sigma/\sigma_0 = \coth a - 1/a,$$

$$\frac{\sigma}{\sigma_0} = \frac{MRT}{\sigma_M^2 \rho N} a = \frac{T}{\theta} \cdot \frac{a}{3}. \quad . \quad . \quad . \quad . \quad (6)$$

The result may be expressed as

$$\sigma/\sigma_0 = f(T/\theta), \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where the function may be found graphically.

The variation of the magnetization near the Curie point may be found analytically by making use of the approximation (1 a). (Near the Curie point, a may be regarded as small.)

$$\sigma/\sigma_0 = a/3 - a^3/45. \quad . \quad . \quad . \quad . \quad (1\,a)$$

Substituting for σ/σ_0 from (6),

$$\frac{a}{3}\left(1-\frac{T}{\theta}\right) = \frac{a^3}{45},$$

$$a = \sqrt{15\left(1-\frac{T}{\theta}\right)}. \quad . \quad . \quad . \quad . \quad (8)$$

As long as T is not much less than θ, the value of σ/σ_0 is given by the first term in (1 a), so that

$$\frac{\sigma}{\sigma_0} = \frac{a}{3} = \sqrt{\frac{5}{3}\left(1-\frac{T}{\theta}\right)}. \quad . \quad . \quad . \quad . \quad (9)$$

If $(\sigma/\sigma_0)^2$ is plotted against (T/θ), the slope of the tangent at the Curie point $(T/\theta=1)$ is $-\frac{5}{3}$,

$$\left[\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}\right]_{T/\theta\to 1}=-\frac{5}{3}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

At very low temperatures $(T/\theta\to 0)$,

$$\sigma/\sigma_0 = 1-1/a.$$

Substituting $\frac{1}{3}\frac{T}{\theta}\frac{\sigma_0}{\sigma}$ for $\frac{1}{a}$ from (6),

$$\frac{T}{\theta}=3\left[\frac{\sigma}{\sigma_0}-\left(\frac{\sigma}{\sigma_0}\right)^2\right]; \quad . \quad . \quad . \quad . \quad (11)$$

$$\left[\frac{d(T/\theta)}{d(\sigma/\sigma_0)}\right]_{T/\theta\to 0}=3-6\left(\frac{\sigma}{\sigma_0}\right)\doteqdot -3,$$

$$\left[\frac{d(\sigma/\sigma_0)}{d(T/\theta)}\right]_{T/\theta\to 0}\doteqdot -\frac{1}{3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Some of the expressions derived above have been given by Debye *, who has shown in particular that the variation in magnetization near absolute zero given by the Langevin theory is incompatible with Nernst's heat theorem, as the entropy tends to an infinite value.

The main quantitative characteristics of the "classical" theoretical curve for the variation of magnetization with temperature are summarized by (10) and (12). The intermediate parts can be obtained with sufficient accuracy graphically, so that a satisfactory comparison with the experimental results may be made.

Quantum Theory.

Quantized systems with a moment $\mu=jg\mu_B$ can assume moments in the field direction equal to $mg\mu_B$, where m has the values $j, j-1, j-2 \ldots -j$. (It may here be noted that for free electrons, and atoms or ions in S states, $g=2$. For electrons, and doublet atoms or ions, $j=\frac{1}{2}$.) The quantum analogue of the Langevin equation is

$$\frac{\bar{\mu}}{\mu}=\frac{\sigma}{\sigma_0}=\frac{1}{jg}\left(\sum_{-j}^{+j}e^{mgh}mg\right)\Big/\left(\sum_{-j}^{+j}e^{mgh}\right), \quad . \quad . \quad (13)$$

where h is written for $\frac{\mu_B H}{kT}$.

* P. Debye, 'Handbuch der Radiologie,' vi. (1925); *Ann. der Phys.* lxxxi. p. 1154 (1926).

The Weiss equation, as before, is

$$a = \frac{\mu H_e}{kT} + \frac{\mu NI}{kT}$$

$$= \frac{\mu H_e}{kT} + \frac{\sigma_M N\rho}{MRT}\bar{\mu}_\mu. \quad . \quad . \quad . \quad (14)$$

Curie Point.—Expanding the exponentials in (13),

$$\frac{\bar{\mu}}{\mu} = \frac{1}{j}\sum_{-j}^{+j} m\left(1+mgh+\frac{(mgh)^2}{2!}+\ldots\right) \Big/ \sum_{-j}^{+j}(1+mgh+\ldots)$$

$$= \frac{1}{j}\sum_{-j}^{+j}\left(m^2gh+m^4\frac{(gh)^3}{3!}+\ldots\right) \Big/ \sum_{-j}^{+j}\left(1+\frac{(mgh)^2}{2!}\ldots\right). \quad (15)$$

The following sums are required :—

$$\left.\begin{aligned} \sum_{-j}^{+j} 1 &= 2j+1, \\ \sum_{-j}^{+j} m^2 &= \tfrac{1}{3}j(j+1)(2j+1), \\ \sum_{-j}^{+j} m^4 &= \tfrac{1}{15}j(j+1)(2j+1)(3j^2+3j-1). \end{aligned}\right\} \quad . \quad . \quad (16)$$

Taking the first approximation (corresponding to $\bar{\mu}/\mu = a/3$ in the classical case),

$$\frac{\mu}{\mu} = \frac{1}{j}\frac{j(j+1)(2j+1)gh}{3(2j+1)}$$

$$= \frac{gh(j+1)}{3}$$

$$= \frac{g\mu_B H(j+1)}{3kT} = \frac{(jg\mu_B)H}{3kT}\cdot\frac{j+1}{j} = \frac{a}{3}\cdot\frac{j+1}{j}. \quad (17)$$

Spontaneous magnetization can occur when the slope of the line (14) with $H_e=0$ is less than the slope of the tangent at the origin to (13), given by (17),

$$\frac{MRT}{\sigma_M{}^2 N\rho} < \frac{j+1}{3j},$$

$$T < \frac{j+1}{3j}\frac{N\rho\sigma_M{}^2}{MR},$$

$$\theta = \frac{j+1}{3j}\frac{N\rho\sigma_M{}^2}{MR}. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The minimum value of $\frac{j+1}{3j}$ is $\frac{1}{3}$ (corresponding to the classical theory); the maximum for $j=\frac{1}{2}$ is 1.

Paramagnetism.—Above the Curie point, and with a small, following the same procedure as before,

$$\chi_{\mathrm{M}} = \frac{\mathrm{L}\bar{\mu}}{\mathrm{H}_e} = \frac{\mathrm{L}^2(jg\mu_{\mathrm{B}})^2}{3\mathrm{R}(\mathrm{T}-\theta)}\frac{j+1}{j} = \frac{\sigma_{\mathrm{M}}^2/3\mathrm{R}}{\mathrm{T}-\theta}\cdot\frac{j+1}{j}$$

$$= \frac{\mathrm{C}_{\mathrm{M}}}{\mathrm{T}-\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

If the values of j and g are known, the value of C_{M} can be calculated. It is convenient, however, for the reasons already given, to obtain an expression for p in terms of j and g.

From (5),

$$p = \frac{1}{\mathrm{M}_{\mathrm{W}}}\sqrt{3\mathrm{RC}_{\mathrm{M}}} = \frac{1}{\mathrm{M}_{\mathrm{W}}}\mathrm{L}jg\mu_{\mathrm{B}}\sqrt{\frac{j+1}{j}}$$

$$= \frac{\mathrm{M}_{\mathrm{B}}}{\mathrm{M}_{\mathrm{W}}}g\sqrt{j(j+1)}$$

$$\doteqdot 5g\sqrt{j(j+1)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This is the well-known expression which has been used so extensively for paramagnetics.

In general there is no simple convenient expression for (13). For $j=\frac{1}{2}$, $g=2$, $\mu=\mu_3$,

$$\frac{\bar{\mu}}{\mu} = \frac{\sigma}{\sigma_0} = \frac{1}{2j}(e^h-e^{-h})(e^h+e^{-h})$$

$$= \tanh(\mu_{\mathrm{B}}\mathrm{H}/k\mathrm{T}) = \tanh a \quad . \quad . \quad . \quad . \quad (21)$$

$$= a-a^3/3+\ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21\,a)$$

Ferromagnetism.—As in the classical case, the curve giving σ/σ_0 as a function of T/θ may be obtained by graphical elimination of a $(=jg\mu_{\mathrm{B}}\mathrm{H}/k\mathrm{T})$ between equations (13) and (14). The curve lies above the classical curve over the whole range, the relative magnetization for a given value of T/θ being greater. For temperatures near the Curie point an analytical procedure may be followed by taking the second approximation for σ/σ_0 from (15). From (15), making use of (16), there results, after reduction,

$$\frac{\bar{\mu}}{\mu} = \frac{\sigma}{\sigma_0} = \frac{j+1}{3j}a - \frac{j+1}{3j}\cdot\frac{2j^2+2j+1}{30j^2}a^3. \quad . \quad . \quad (22)$$

From (14) for $H_e=0$, using (18), the second equation is

$$\frac{\bar{\mu}}{\mu}=\frac{T}{\theta}\cdot\frac{j+1}{3j}a. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Combining these equations,

$$\frac{j+1}{3j}a\left(1-\frac{T}{\theta}\right)=\frac{j+1}{3j}\cdot\frac{2j^2+2j+1}{30j^2}a^3,$$

$$a=\sqrt{\left\{\frac{30j^2}{2j^2+2j+1}\left(1-\frac{T}{\theta}\right)\right\}}. \quad . \quad . \quad (24)$$

Using the first term approximation in (22),

$$\left(\frac{\sigma}{\sigma_0}\right)_{T/\theta\to 1}=\sqrt{\left\{\frac{10}{3}\frac{(j+1)^2}{j^2+(j+1)^2}\left(1-\frac{T}{\theta}\right)\right\}}. \quad . \quad (25)$$

The quantum expression corresponding to (10) is

$$\left[\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}\right]_{T/\theta\to 1}=-\frac{10}{3}\frac{(j+1)^2}{j^2+(j+1)^2}. \quad . \quad . \quad (26)$$

This has a minimum (numerical) value (for $j\to\infty$) of 5/3 and a maximum (for $j=\frac{1}{2}$) of 3. At very low temperatures, for this same limiting case

$$\frac{\sigma}{\sigma_0}=\tanh a=\frac{e^a-e^{-a}}{e^a+e^{-a}}\doteq 1-2e^{-2a}. \quad . \quad . \quad (27)$$

Since a becomes very large as $T/\theta\to 0$,

$$\left[\frac{d(\sigma/\sigma_0)}{d(T/\theta)}\right]_{T/\theta\to 0}=0. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

In general a limiting value for σ/σ_0 as T/θ approaches zero may be found by taking the first two terms in the expansion of (13),

$$\left(\frac{\sigma}{\sigma_0}\right)_{a\gg 1}=\frac{1}{j}\frac{je^{jgh}+(j-1)e^{(j-1)gh}+\ldots}{e^{jgh}+e^{(j-1)gh}+\ldots}$$

$$\doteq\left(1-\frac{j-1}{j}e^{-gh}\right)(1-e^{-gh})$$

$$=1-\frac{1}{j}e^{-gh}.$$

Since $h=\mu_3 H/kT$, $gh=gj\mu_B H/jkT=\frac{a}{j}$,

$$\left(\frac{\sigma}{\sigma_0}\right)_{a\gg 1}=1-\frac{1}{j}e^{-aj}, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

in agreement with (27) for $j=\frac{1}{2}$.

TABLE I.—Classical and Quantum Theory Formulæ for Para- and Ferromagnetism.

	Classical Theory.	Quantum Theory.	
		General.	$[j=\frac{1}{2} \quad g=2.$
Paramagnetism. θ	$\frac{1}{3}\cdot\frac{N\rho\sigma_M^2}{MR}$	$\frac{j+1}{3j}\cdot\frac{N\rho\sigma_M^2}{MR}$	$\frac{N\rho\sigma_M^2}{MR}$
$p=14{\cdot}07\sqrt{C_M}$	$\frac{\mu}{\mu_W}$	$\frac{\mu}{\mu_W}\sqrt{\frac{j+1}{j}}=5g\sqrt{j(j+1)}$	$\frac{\mu_B}{\mu_W}\sqrt{3}=8{\cdot}6$
$\frac{\sigma}{\sigma_0}$	$\coth a-\frac{1}{a}$	Eq. (13)	$\tanh a$
$\frac{\sigma}{\sigma_0}\quad(a\ll 1)$	$\frac{a}{3}-\frac{a^3}{45}$	$\frac{j+1}{3j}a-\frac{j+1}{3j}\cdot\frac{2j^2+2j+1}{30j^2}a^3$	$a-\frac{a^3}{3}$
$\frac{\sigma}{\sigma_0}\quad(a\gg 1)$	$1-\frac{1}{a}+2e^{-2a}$	$1-\frac{1}{j}e^{-\frac{a}{j}}$	$1-2e^{-2a}$
Ferromagnetism. $\frac{\sigma}{\sigma_0}\quad\left(\frac{T}{\theta}\to 1\right)$	$\sqrt{\left\{\frac{5}{3}\left(1-\frac{T}{\theta}\right)\right\}}$	$\sqrt{\left\{\frac{10}{3}\frac{(j+1)^2}{j^2+(j+1)^2}\left(1-\frac{T}{\theta}\right)\right\}}$	$\sqrt{\left\{3\left(1-\frac{T}{\theta}\right)\right\}}$
$\left[\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}\right]_{T/\theta\to 1}$	$-\frac{5}{3}$	$-\frac{10(j+1)^2}{3\{j^2+(j+1)^2\}}$	-3
$\left[\frac{d(\sigma/\sigma_0)}{d(T/\theta)}\right]_{T/\theta\to 1}$	$-\frac{1}{3}$	0	0

The slope of the tangent for $T/\theta=0$ will in all cases be zero.

The main formulæ for para- and ferromagnetism which have been derived in this section are collected together in Table I.

The Change in Specific Heat at the Curie Point.

The essential postulate of Weiss that there is a pseudo-magnetic field NI in ferromagnetics may also be stated, as he has pointed out, in the form that the energy associated with magnetization in ferromagnetics is large and negative, being equal to $-\frac{1}{2}NI^2$ per unit volume. The specific heat associated with the change in this "magnetic" energy is given by

$$S=-\frac{d}{dT}\frac{1}{2}\left(\frac{NI^2}{\rho}\right)$$

$$=-\frac{1}{2}N\rho\frac{d\sigma^2}{dT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

For the "magnetic" specific heat per gram molecule S_M,

$$S_M=-\frac{1}{2}N\rho M\frac{d\sigma^2}{dT}$$

$$=-\frac{1}{2}N\rho M\sigma_0^2\frac{d}{dT}\left(\frac{\sigma}{\sigma_0}\right)^2$$

$$=-\frac{1}{2}\frac{N\rho\sigma_M^2}{M\theta}\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}. \quad . \quad . \quad . \quad . \quad (31)$$

From the values for θ in Table I. this gives

$$\text{Classical Theory ...} \quad S_M=-\frac{3R}{2}\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}, \quad . \quad . \quad . \quad . \quad (32)$$

$$\text{Quantum Theory...} \quad S_M=-\frac{3jR}{2(j+1)}\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}. \quad . \quad . \quad (33)$$

Above the Curie point, θ, the spontaneous magnetization becomes zero, and the decrease ΔS_M in specific heat on passing through θ is equal to S_M calculated from the value of $\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}$ just below the Curie point.

$$\text{Classical Theory ...} \quad (\Delta S_M)_{T=\theta}=\frac{5R}{2}, \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$\text{Quantum Theory...} \quad (\Delta S_M)_{T=\theta} = \frac{5R}{2} \frac{j^2+j}{j^2+j+\frac{1}{2}}. \quad . \quad . \quad (35)^*$$

For the purposes of this calculation it has been supposed that one carrier of moment μ (or $jg\mu_B$) is associated with each molecule (or atom). Taking $R = 2$, the values of ΔS_M for various values of j in calories per gram molecule are shown in Table II. The classical formula corresponds to $j \to \infty$ in the quantum formula.

TABLE II.

Change in Specific Heat at the Curie Point in Calories per Gram Molecule.

j	½	1	3/2	2	5/2	3	$\to\infty$
ΔS_M.....	3	4	4·41	4·61	4·73	4·8	5

Unless the treatment has to be essentially modified in the light of the Heisenberg theory, the indications are that if the decrease in the gram atomic heat is less than 3 (as for nickel), there must be less than one independent carrier per atom; and that if the decrease—attributable to the magnetic change only—is greater than 5 (as for iron), there must be more than one quasi-independent carrier per atom.

Heisenberg's Theory of Ferromagnetism.

In his theory Heisenberg† investigates the effect of interchange interaction in a lattice consisting of similar atoms, each atom containing one electron free to orientate itself. The magnetization is attributed to these electrons, the remainder of the atom having no magnetic effect. (This assumption is perhaps somewhat artificial; but the interaction of atoms having one electron in excess of a closed configuration will presumably be similar to that of atoms which have one electron less than the number required to complete a group ‡. These correspond more closely to the atoms (or ions) of the ferromagnetic elements, in which the *d*-group of electrons is incomplete.) It is shown that if the interaction integral is positive, spontaneous magnetization

* This formula is quoted by J. Dorfmann and I. Kikoin, *Zeits. für Phys.* liv. p. 289 (1929).

† W. Heisenberg, *Zeits. für Phys.* xlix. p. 619 (1928).

‡ *Cf.* J. E. Lennard-Jones, Trans. Faraday Soc. xxv. p. 683 (1829).

may occur below a critical temperature, the model having the salient characteristics of a ferromagnetic. Before considering certain points in the treatment in greater detail, the results will be written down in a form which enables them to be compared with those from previous theories. Since the carriers are electrons, the equations are most usefully compared with (13) and (14) in their simplest forms (13 in the form 21). Heisenberg's results may be expressed by the equations

$$\bar{\mu}/\mu = \sigma/\sigma_0 = \tanh a, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$a = \frac{\mu H_e}{kT} + \frac{1}{2}\left(\beta - \frac{\beta^2}{z}\right)\frac{\bar{\mu}}{\mu} + \frac{\beta^2}{4z}\left(\frac{\bar{\mu}}{\mu}\right)^3, \quad . \quad . \quad (37)$$

where

$\beta = zJ_0/kT$,

z = number of neighbours surrounding each atom. ($z=8$ for a cube-centred lattice, $z=12$ for a face-centred lattice),

J_0 = interaction integral.

When the external field is zero the Weiss equation

$$a = \frac{N\rho\sigma_M^2}{MRT}\frac{\bar{\mu}}{\mu}$$

is replaced by

$$a = \frac{1}{2}\left(\beta - \frac{\beta^2}{z}\right)\frac{\bar{\mu}}{\mu} + \frac{\beta^2}{4z}\left(\frac{\bar{\mu}}{\mu}\right)^3$$

Substituting I_0 for $\rho\sigma_M/M$, and μ/k for σ_M/R, and zJ_0/kT for β, the constant NI_0 of the Weiss theory (giving the maximum molecular field) is replaced by

$$\frac{1}{2\mu}\left[zJ_0\left\{1 - \frac{J_0}{kT} + \frac{J_0}{2kT}\left(\frac{\bar{\mu}}{\mu}\right)^2\right\}\right], \quad . \quad . \quad (39)$$

a quantity which varies with the magnetization and with the temperature.

Following the same treatment as before, spontaneous magnetization occurs for

$$\frac{1}{2}\left(\beta - \frac{\beta^2}{z}\right) > 1. \quad . \quad . \quad . \quad . \quad . \quad (40)$$

This is a maximum when $\beta = \frac{z}{2}$, so that, as a necessary condition,

$$z \geqq 8.$$

In general the limiting values of β for which spontaneous magnetization will occur are given by the roots of the equation

$$\beta^2-4\beta z+2z=0.$$

$$\beta=\tfrac{1}{2}\{z\pm\sqrt{z^2-8z}\}$$

$$=\frac{z}{2}\left\{1\pm\sqrt{1-\frac{8}{z}}\right\},$$

giving

$$T=\frac{2J_0}{k\left\{1\pm\sqrt{1-\frac{8}{z}}\right\}}. \quad . \quad . \quad . \quad (41)$$

As the temperature decreases from a high value, spontaneous magnetization will set in when

$$T=\frac{2J_0}{k\left\{1-\sqrt{1-\frac{8}{z}}\right\}},$$

increase to a maximum roughly at

$$T=\frac{2J_0}{k},$$

then decrease, and disappear when

$$T=\frac{2J_0}{k\left\{1+\sqrt{1-\frac{8}{z}}\right\}}.$$

In the limiting case when $z=8$ the two values of T are equal, and spontaneous magnetization will just not occur, or taking into account the higher terms, will be restricted to the neighbourhood of the Curie point. In any case the range in which spontaneous magnetization occurs will be small. The behaviour of actual ferromagnetics is, of course, widely different from that indicated by the Heisenberg equations in their present form.

The Change in Specific Heat at the Curie Point.—Below the Curie point, in the absence of an external field, the part of the energy dependent on the magnetization per gram atom is given by

$$(E_A)_I=-RT\left\{\frac{1}{4}\left(\beta-\frac{2\beta^2}{z}\right)\left(\frac{\bar{\mu}}{\mu}\right)^2+\frac{\beta^2}{8z}\left(\frac{\bar{\mu}}{\mu}\right)^4\right\}. . \quad (42)$$

From this and the equations for the magnetization (36) and (37), the part of the specific heat associated with the magnetization may be determined. Fowler and Kapitza * conclude that the change at the Curie point will be roughly

$$\Delta S_A = \tfrac{3}{2} R. \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

They reach this conclusion, however, by making use of some approximations which do not seem justifiable. In the neighbourhood of the Curie point the term in $(\mu/\mu)^4$ may be neglected, and there results for the change in specific heat

$$\Delta S_A = -R\theta\left[\tfrac{1}{4}\beta\left(1-\frac{2\beta}{z}\right)\right]\left\{\frac{d}{dT}\left(\frac{\sigma}{\sigma_0}\right)^2\right\}_{T=\theta}$$

$$= -R\left[\tfrac{1}{4}\beta\left(1-\frac{2\beta}{z}\right)\right]\left\{\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)}\right\}_{T=\theta}.$$

Making use of (36) and (37),

$$\Delta S_A = 3R\left[\tfrac{1}{4}\beta\left(1-\frac{2\beta}{z}\right)\right]. \quad . \quad . \quad . \quad . \quad (44)$$

Fowler and Kapitza state that the factor in square brackets is approximately $\frac{1}{2}$. From the equations (41), however,

$$\beta_{T=\theta} = \frac{z}{2}\left\{1-\sqrt{1-\frac{8}{z}}\right\}.$$

Substituting in (44),

$$\Delta S_A = \tfrac{3}{2} R\left[\frac{z}{8}\left\{1-\sqrt{1-\frac{8}{z}}\right\}\left(\sqrt{1-\frac{8}{z}}\right)\right]. \quad (45)$$

This gives the results

$$z = 8, \quad \Delta S_A = 0,$$

$$z = 12, \quad \Delta S_A = \tfrac{3}{2} R\left[\tfrac{1}{2}(\sqrt{3}-1)\right] = \cdot 55\, R.$$

Such agreement with experiment as is given by (43) thus completely disappears.

Energy Distribution of States.—The lack of agreement between theory and experiment in respect both of magnetization and the change in specific heat can be traced to the occurrence of terms in β^2 in (37). In discussing the magnetization, Heisenberg suggests that the failure of the theory for lower temperatures is possibly due to the special assumptions made as to the energy distribution of

* R. H. Fowler and P. Kapitza, Proc. Roy. Soc. cxxiv. p. 1 (1929).

states corresponding to a particular value for the number of unpaired electrons.

While it is unnecessary here to outline the whole treatment—for which Heisenberg's paper or that of Fowler and Kapitza should be consulted—it seems desirable to indicate briefly how the $\mathcal{B}^2$ terms arise. The nomenclature of the papers referred to will be followed as far as possible.

Let $2n$ be the number of atoms, each with one electron free to orientate itself, J_0 the interchange interaction integral. The atoms are treated as hydrogen-like, but J_0 must be positive (it is negative for two hydrogen atoms in the ground state) in order that the corresponding energy may be negative when the spins are parallel. Each atom is surrounded by z neighbours. Each electron has a spin of $\frac{1}{2}$ and a magnetic moment of 1 in Bohr units. Each arrangement of $(n-s)$ pairs of electrons (with zero resultant spin) and $2s$ unpaired electrons corresponds to a term with a resultant moment s. Using the suffix σ to refer to this partition, that is to

$$2+2+2 \ldots (n-s) \text{ times}\,;\quad 1+1+1 \ldots 2s \text{ times},$$

it may be shown that the number of such arrangements, or terms, is f_σ where

$$f_\sigma = \frac{2n!}{(n+s)!\,(n-s)!} - \frac{2n!}{(n+s+1)!\,(n-s-1)!}, \quad (46)$$

and the mean energy depending on interchange interaction is E_σ where

$$E_\sigma = -z\frac{s^2+n^2}{2n}J_0. \quad (47)$$

The energy of these terms will be distributed about this mean value, and the mean square deviation Δ_σ^2 may further be shown to be

$$\Delta_\sigma^2 = zJ_0^2\frac{(n^2-s^2)(3n^2-s^2)}{4n^3}. \quad (48)$$

It is here that the particular assumption is made that the distribution is Gaussian, and that the number of terms with energies between $E_\sigma + x$ and $E_\sigma + x + dx$ is

$$\frac{f_\sigma}{\sqrt{2\pi}\Delta_\sigma}e^{-\frac{1}{2}x^2/\Delta_\sigma^2}dx.$$

In the summand of the partition function there then appears the factor

$$\exp\{E_\sigma/kT + \Delta_\sigma^2/(2k^2T^2)\}. \quad (50)$$

The stable state of magnetization is obtained by finding the value for which the summand is a maximum, with the result given by (36) and (37), the β^2 terms in (37) coming from the Δ_σ^2 term in (50).

The equations (48) and (49) imply that some of the states corresponding to a spin s ($s < n$) will have an energy less than that for $s=n$. Expressed in another way this means that states of small magnetization are assumed possible for which the energy is less than that corresponding to saturation magnetization. Since $\Delta_\sigma=0$ for $s=n$ from (48), and $f_\sigma=1$ from (46), the most probable state giving an energy equal to that for saturation will correspond to a magnetization less than the saturation value. This illustrates, by the consideration of a special case, how the variation of magnetization with temperature—already discussed—is linked up with the energy deviations and their assumed distribution.

The difficulty seems to be inherent in the group theory method of treating the crystal as a whole. The root mean square deviation is always small compared with the energy. When s is small, for example,

$$E_\sigma = -znJ_0/2, \quad \text{and} \quad \sqrt{\overline{\Delta_\sigma^2}} = J_0\sqrt{3nz}/4.$$

On the other hand, the deviation will in general be large compared with kT, and it is this which gives the β^2 terms their importance at the lower temperatures. It should be noted, however, as shown by the consideration of the specific heat change, that it is not only at lower temperatures that the β^2 terms are in disagreement with experiment.

Modified Treatment *.—Instead of the crystal being treated as a whole, it may be regarded for approximate purposes as an assembly of atoms. The electron free to orientate itself in each atom can set itself parallel or antiparallel to the direction of magnetization of the crystal. The energy in these two settings is $\pm \frac{zJ_0}{z}\frac{\bar{\mu}}{\mu}$. The expression then obtained for the magnetization is

$$\frac{\bar{\mu}}{\mu} = \tanh\frac{zJ_0}{2kT}\frac{\bar{\mu}}{\mu} \quad . \quad . \quad . \quad . \quad . \quad (51)$$

$$= \tanh\frac{\beta}{2}\frac{\bar{\mu}}{\mu}.$$

* E. C. Stoner, Proc. Leeds Phil. Soc. ii. p. 56 (1930).

The result is formally the same as that given by the Weiss theory, modified for the quantum $j=\frac{1}{2}$ case, the molecular field constant being interpreted as $zJ_0/2\mu I_0$. While the rigour of the treatment is perhaps open to question, it does show in a simple way how interchange interaction may give rise to molecular field effects, and the difficulties which arise in dealing with energy fluctuations of a crystal are evaded. Moreover, as will be indicated in the next section, this equation is in close agreement with the present results of ferromagnetics.

Experimental Results on Ferromagnetics.*

The fundamental problems of ferromagnetism are those connected with the nature of the carriers and of the molecular field, and a large number of the experimental results on ferromagnetics are of secondary importance from this point of view. In this section some of the results which are of importance in connexion with the theories which have been discussed will be very briefly summarized, and their significance will be indicated.

Gyromagnetic Effect.—The experiments on the gyromagnetic effect show conclusively that in ferromagnetics at ordinary temperatures the ratio of the magnetic to the mechanical moment of the carriers is 2, both moments being measured in Bohr units. This, taken by itself, is consistent with the view that the carriers are (1) free electrons, (2) atoms or ions in S states, or (3) electrons in atoms or ions free to change their orientation. When atoms are in S states, the moment is entirely due to the spin moment s of the electron ; the third possibility differs from the second in that the atom or ion may have an "orbital" moment, but that this is assumed to be ineffective magnetically owing to some kind of "l interlocking" of the different atoms.

Variation of "Spontaneous magnetization" with Temperature below the Curie Point.—When (σ/σ_0) is plotted against (T/θ) the curves for iron, cobalt, and nickel differ little from each other, and lie well above the curve given by the Langevin-Weiss theory. The results of Weiss and Forrer† for nickel are probably the most accurate. The experimental curve has been carefully compared by Tyler ‡ with those given by

* For references see E. C. Stoner, 'Magnetism and Atomic Structure,' 1926, and 'Magnetism,' 1930 (Methuen).

† P. Weiss and R. Forrer, *Ann. de Phys.* v. p. 153 (1923).

‡ F. Tyler, Phil. Mag. ix. p. 1026 (1930).

the modified Weiss theory for the various quantum cases; it is in good agreement with the curve corresponding to $j=\frac{1}{2}$, and is quite definitely incompatible with the classical curve, or the quantum curves for higher values of j. The experimental curve lies slightly below the theoretical for $T/\theta \to 0$ and slightly above for $T/\theta \to 1$; these discrepancies may be of significance, but they are small, and the conclusion can be drawn that to a close approximation the experimental results for the three ferromagnetic elements correspond to magnetic carriers for which $j=\frac{1}{2}$. The conclusion as to the carriers is the same as that to be derived from a consideration of a gyromagnetic effect. The form of the magnetization temperature curve is incompatible with the Heisenberg formula, obtained by treating the crystal as a whole, but agrees with that obtained by the modified treatment of the interchange interaction, in which the atoms in the crystal are regarded as separate systems; this suggests that if the "whole crystal" method is used, the treatment of fluctuations requires considerable modification

Change of Specific Heat at the Curie Point.—If the carriers are identified as electrons, and there are f of these per atom, the change in the gram atomic specific heat at the Curie point will be

$$\Delta S_A = \tfrac{3}{2} R f = 3f. \quad . \quad . \quad . \quad . \quad . \quad (52)$$

This follows from the "quantized" Weiss theory (eq. 35) or from the interchange interaction theory, as expressed by (51), but not from the original Heisenberg formula, which leads to (45).

Now f is obtainable directly from the value of the saturation magnetization. If p is the atomic moment (from saturation) expressed in Weiss units, since the electron moment corresponds to 5 Weiss units

$$f=\frac{p}{5}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

If there is no change in the number of "magnetic electrons" between low temperatures and the Curie point, the same value for f should be obtained from (52) and (53). The results for iron and nickel are shown in Table III.

The agreement in the f values derived in the two ways can leave little doubt that the carriers are electrons (or more precisely that it is the spin moment of electrons which is effective); it also shows that the number of

magnetic electrons changes very little, if at all, between low temperatures and the Curie point.

Thermoelectric Properties.—Dorfmann and Jaanus* have recently measured carefully the thermoelectric power of nickel against platinum over a range of temperatures. Their results show that there is a fairly sudden change in the Thomson coefficient for nickel at the Curie point. They have interpreted this as indicating that there is a change in the specific heat of the conduction electrons; and if this view is taken, the magnitude is such that the whole change in the specific heat of nickel at the Curie

TABLE III.

Number of Magnetic Electrons per atom from Low Temperature Magnetization and Change in Specific Heat.

			f.	
	p.	ΔS_A.	*p*/5.	$\Delta S_A/3$.
Ni	3	1·7	0·60	0·57
Fe	11	6·8	2·20	2·27

point can be attributed to the change in that of the conduction electrons. It is doubtful whether this interpretation can be maintained; but in any case other considerations † show that the ferromagnetism cannot be due to electrons which are free in the Sommerfeld sense, and the results do not necessarily conflict with the view that ferromagnetism is to be traced to electrons "in atoms" as in Heisenberg's theory.

Susceptibility above the Curie Point.—The possible significance of the temperature variation of susceptibility above the Curie point has been discussed elsewhere ‡. It will be

* J. Dorfmannl, R. Jaanus, and I. Kikoin, *Zeits. für Phys.* liv. pp. 277 & 289 (1929).

† F. Bloch, *Zeits. für Phys.* lvii. p. 545 (1929); E. C. Stoner, Proc. Leeds Phil. Soc. ii. p. 50 (1930).

‡ E. C. Stoner, Proc. Leeds Phil. Soc. i. p. 55 (1926).

sufficient here to consider some of the values for iron. If there are f magnetic electrons per atom (that is, f effectively independent spin moments) the value of f can be calculated in terms of p_A, the magneton value per atom, calculated as in (5). Writing p_e for the magneton value per electron,

$$p_A^2 = f \times p_e^2.$$

Using (20),

$$p_A^2 = f \times \{5g\sqrt{j(j+1)}\}^2$$
$$= f \times (5\sqrt{3})^2,$$
$$f = \frac{1}{3}\left(\frac{p_A}{5}\right)^2.$$

In Table IV. are given the values of f, so calculated for various states of iron.

TABLE IV.

Values of f from Paramagnetic Susceptibility.

	p_A.	f.
Fe β_1.....	20·9	5·8
β_2...	17·4	4·0
γ	28·2	10·6
δ	7·05	0·7

It is hardly possible to suppose that the number of quasi-independent effective spin moments per atom could change in this manner, and that the number could be as large as 10. The only possible conclusion seems to be that above the Curie point the orbital moments l may play a part as well as the s moments, and the magnetization may then be said to be due to ions (or atoms) as carriers rather than to individual electrons in them. This point of view has already been put forward * and will not be further discussed here.

The experimental evidence as a whole supports the view that the carriers in ferromagnetics are electrons in atoms, the interchange interaction electrons of Heisenberg's theory.

* E. C. Stoner, Phil. Mag. viii. p. 250 (1929).

The detailed results of that theory are not in agreement with the observations on ferromagnetics. The observations do, however, agree well with the formal formulæ given by the quantum modification of the Weiss theory for the $j=\frac{1}{2}$ case, and by a slight change in the treatment of the interaction theory it may be shown that the Weiss molecular field constant is very simply related to the interaction integral.

Summary.

Formulæ for the variation of magnetization with field and temperature are derived, using the quantum modification of the formal Weiss theory of ferromagnetism. These are put into such a form as to facilitate comparison with experiment. The more important are collected in a table. Expressions for the change in specific heat at the Curie point are also given.

The Heisenberg interchange interaction theory is discussed. It leads to a satisfactory interpretation of the molecular field, but gives quantitative results which cannot be reconciled with experiment for the variation of spontaneous magnetization with temperature and for the change in specific heat. This is due to difficulties in the treatment of "fluctuations." If the crystal, instead of being treated as a whole, is regarded as an aggregate of atomic systems, a result is obtained which is formally similar to that of Weiss, modified for the quantum $j=\frac{1}{2}$ case, the molecular field constant N being replaced by $z\mathrm{J}_0/2\mu\mathrm{I}_0$.

The gyromagnetic ratio and the variations of magnetization with temperature indicate that magnetization in ferromagnetics is due to the change of orientation of electrons. The saturation magnetization and the change in specific heat lead to the same value for the number of effective electrons per atom. This indicates that the number of these electrons varies little up to the Curie point. Above the Curie point the variation of susceptibility with temperature leads to magnetic moments per atom which cannot be entirely attributed to the electron spin moments (s), but must be partly due to the orbital moments (l). Below the Curie point, all the experimental results are compatible with the view that the primary magnetic characteristics are due to the interchange interaction electrons, whose spin moments only are magnetically effective.

Physics Department,
University of Leeds.
March 1930.

IV. *Inductive Ratio Arms in Alternating Current Bridge Circuits.* *By* R. Walsh, *B.Sc.* (International Telephone and Telegraph Laboratories Incorporated, Hendon.) *

Introduction.

In the practice of alternating current measurement the Wheatstone net is perhaps the most widely used of all devices, and in the course of many years of development the Wheatstone Bridge has been made an instrument of high precision. The chief difficulties which have been encountered in obtaining high accuracy have been concerned with the stray capacities in the circuit and the balance of the ratio arms.

This paper gives a theoretical account of a new type of ratio arms assembly intended to give high stability and high accuracy, which it is hoped will contribute to practical bridge design by rendering more simple the questions of construction and maintenance.

To avoid confusion of terms, it is here convenient to define the various forms of inductively-wound coils that enter into this investigation. They may be distinguished as follows :—

(*a*) An "inductance coil" is any coil so wound as to possess inductive impedance between its terminals.

(*b*) A "transformer" comprises two or more windings which serve the purpose of providing electromagnetic coupling between two or more independent circuits.

(*c*) A "retardation coil" or "retard coil" is a coil of high impedance. It may have divisions in its windings. It has a high ratio between its alternating current impedance and its direct current resistance.

The difficulties of making non-inductive ratio arms are well known, and a large amount of work has been done both as regards the nature of the windings and the method of construction.

The present method departs radically from classical practice in that the bridge ratio is determined by reactive impedances, these being in the form of bifilar windings on a single core.

The essential ideas connected with the use of such highly balanced coils for bridge measurements have been investigated by A. D. Blumlein.

* Communicated by R. Appleyard.

1. Theoretical Considerations.

1.10. *Ratio Arms and the Bridge Network.*

In the simple case of a Wheatstone net the condition of balance is

$$\frac{Z_{AB}}{Z_{BC}} = \frac{Z_1}{Z_2}$$

(see fig. 1 *a*). Therefore, at balance, the ratio between the impedance Z_1 and Z_2, that is, in general between the standard and the unknown, is determined by the ratio between the two adjacent arms Z_{AB} and Z_{BC}. This applies equally well for non-reactive resistances and for complex impedances.

Fig. 1 *a*. Fig. 1 *b* Fig. 1 *c*.

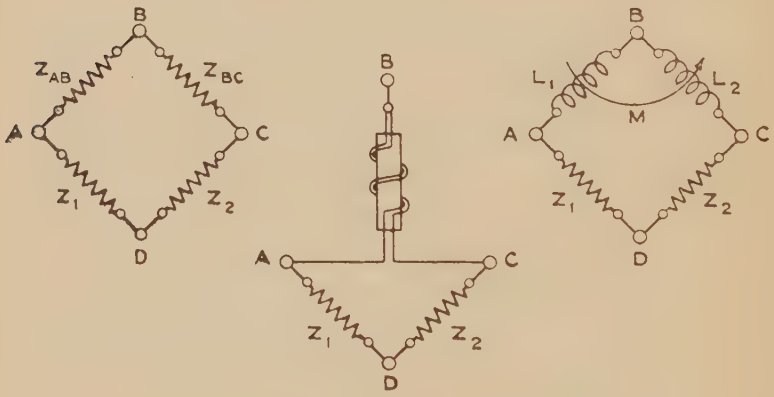


Fig. 1 *a*.—Wheatstone bridge network.
Fig. 1 *b*.—Bridge network with inductive ratio arms.
Fig. 1 *c*.—Simplified arrangement of bridge arms.

1.11. *Retard Coil as Ratio Arms.*

If the windings of a retard coil are used to provide the impedances Z_{AB} and Z_{BC} there will be a mutual inductance M between the arms AB and BC, in addition to their self-impedances.

The arrangement will then be as shown in fig. 1 *b*, and this can be represented more clearly as in fig. 1 *c*.

The balance conditions for such a network are given by the generalized solution of the Wheatstone net*. For the purpose of discussion, however, it is more convenient to use

* B. Hague, 'Alternating Current Bridge Methods,' p. 51.

a well-known transformation in order to remove the complications* due to the mutual inductance between the arms AB and BC.

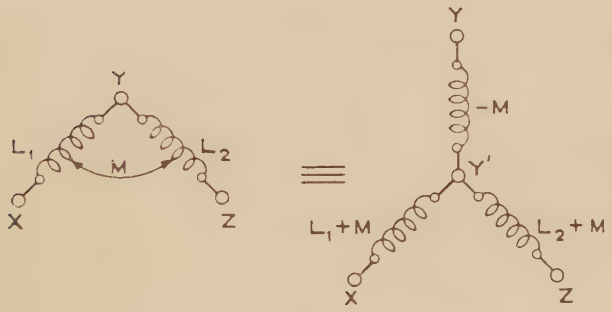
1.12. *Equivalent Ratio Arms without Mutual Inductance.*

The following transformation provides a network which may be considered as exactly equivalent to the original, but which contains no mutual inductance.

The transformation is shown below.

The above transformation (see Hague, 'Alternating Current Bridge Methods,' p. 50) may be directly applied to the Wheatstone net previously shown, which then becomes as in fig. 3.

Fig. 2.



Transformation for mutual inductance.

In practice the impedances

$$R_1+j\omega(L_1+M) \quad \text{and} \quad R_2+j\omega(L_2+M)$$

will be complicated by the presence of an effective resistance term due to iron losses and eddy current losses in the coil windings, but it is not necessary to introduce these considerations into the discussion, because they may be eliminated by considering M to be a complex quantity. This is indeed a necessity of the transformation given above, if the equivalent of the two circuits is to hold for practical inductance coils. The present mode of treating the network of the inductance coil windings is, however, adequate to deal with the principal

* R Appleyard, "The Solutions of Net-work Problems by Determinants," Proc. Phys. Soc. Lond. xxiv. pt. 4 (June 15, 1912).

sources of error, and further analysis will not be attempted in this paper.

The conditions for balance in a Wheatstone Bridge, *i. e.*, for zero potential difference between points A and C, may be defined solely in terms of the impedance of the four arms AB, BC, CD, and DA, and, therefore, the impedance $-j\omega M$ which has appeared in the arm B′D will have no influence in determining the point of balance of the bridge.

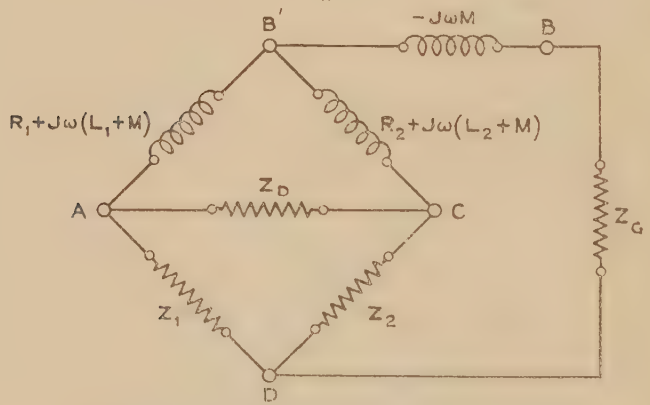
Since at the point of balance

$$\frac{Z_{AB'}}{Z_{B'C}} = \frac{Z_{AD}}{Z_{CD}},$$

the ratio of Z_{AD} to Z_{CD} will depend on the ratio of the two impedances

$$R_1 + j\omega(L_1 + M) \quad \text{and} \quad R_2 + j\omega(L_2 + M).$$

Fig. 3.



Bridge network with mutually inductive ratio arms.

This is exactly the same result as would be obtained by considering a bridge network (fig. 1 *a*) having arms AB and BC composed of separate impedances, in the case of the usual types of ratio arms, having the values given above.

The above reasoning shows how two impedances in adjacent arms of a bridge, and having mutual inductance between them, will determine the ratio of the two remaining arms when the bridge is balanced.

In order to use such an arrangement to make accurate measurements, it must be possible rigidly to control the ratio between the two impedances

$$R_1 + j\omega(L_1 + M) \quad \text{and} \quad R_2 + j\omega(L_2 + M).$$

In order that a bridge made on this principle should be useful in practice, it is necessary that this ratio should be accurately an integer and that it should be as nearly as possible wholly real.

In the further discussion the general case outlined above will be dealt with as two cases—one in which the ratio between the bridge arm impedance is 1 : 1, and the other in which this ratio is $n : 1$, where n is an integer.

In considering a Wheatstone net to be used as a measuring instrument, there is another important aspect which will be affected when inductive windings with mutual inductance between them are substituted for the normal resistance ratio arms, namely, sensitivity. This quality of the bridge network is affected by the values of the impedances of all the branches of the structure, and therefore the presence of the impedance $-j\omega M$ in the generator arm (see fig. 3) must be considered.

If the ratio of the impedance of the Arms AB′ and B′C is theoretically exact, then the potential difference occurring between A and C may be considered as due to an inaccuracy in the ratio of the other two arms AD and CD. The value of this potential difference will, moreover, depend on the degree of the above inaccuracy and the current flowing into the bridge at B′ and D. Thus, in order to make the potential difference as large as possible for a given departure in the ratio Z_{CD} to Z_{AD} from its true balance value, the current into the bridge should be made as large as possible. If no limit is imposed on the value of this current by the conditions of measurement, it will depend on the value of the impedance of the bridge network between the terminals B and D.

In the case of a bridge (fig. 1 *a*) with independent impedances

$$R_1 + j\omega(L_1 + M) = Z_{AB} \quad \text{and} \quad R_2 + j\omega(L_2 + M) = Z_{BC}$$

as ratio arms, the impedance of the bridge network between the terminals B and D will be

$$\frac{Z_{AB} \cdot Z_{BC}}{Z_{AB} + Z_{BC}} + \frac{Z_1 \cdot Z_2}{Z_1 + Z_2},$$

whereas with a retard coil giving equivalent values for the impedance of the ratio arms the value will be

$$\frac{R_1 \cdot R_2}{R_1 + R_2} + \frac{Z_1 \cdot Z_2}{Z_1 + Z_2},$$

owing to the fact that the parallel opposing inductance of the windings of the retard coil is zero.

Since $\frac{R_1 . R_2}{R_1 + R_2}$, the D.C. resistance of the coil windings in parallel, will be a small quantity, it will be seen that the impedance of the bridge circuit between terminals B and D will be considerably less when a retardation coil is used in place of the usual resistances.

On the other hand, if the current to be supplied to the bridge (fig. 3) by the generator is limited by the conditions of measurement, then the sensitivity of the bridge will depend on the current in the detector for a given unbalance potential across AC. Current may flow from A to C by three paths, directly through the detector circuit, *viâ* the point B′ or *viâ* the point D. In order that the maximum proportion may take the direct route, the series aiding impedance of the windings AB′, B′C of the retardation coil should be as high as possible. Owing to the bifilar method of winding these coils, there is a limit to the impedance to which they can be wound ; moreover, it is important, as will be seen later, that the direct-current resistance of the windings be kept as low as possible. Compromise must therefore be made in designing coils for this purpose between the requirements imposed by the questions of balance and sensitivity.

It will be seen that the impedance of the equivalent ratio arms formed by the coil windings depends on the frequency of the testing current employed. Therefore the design of the coil must be adapted to the frequency range within which it will be required to work. If the impedance to be measured is small, or if an unequal ratio bridge is to be used, the impedance which the bridge circuit presents to the generator will be small, and the input to the bridge should be by means of a transformer of suitable ratio in order to secure the maximum efficiency.

The transformation given in Section 1.11 may also be used to make clear the action of a retardation coil when used to provide an unequal ratio.

If, in fig. 3, $L_2 = n^2 L_1$, then the two arms of the equivalent bridge network will have impedances

$$R_1 + \omega L_1 + \omega n \sqrt{L_1^2}$$

and

$$R_2 + n^2 \omega L_1 + \omega n \sqrt{L_1^2},$$

and these reduce to

$$R_1 + j\omega L_1 (1 + n)$$

and

$$R_2 + j\omega n L_1 (1 + n),$$

and it may be seen that, if R_2 is made equal to nR_1, the total impedance of the arms will be in the ratio $n : 1$.

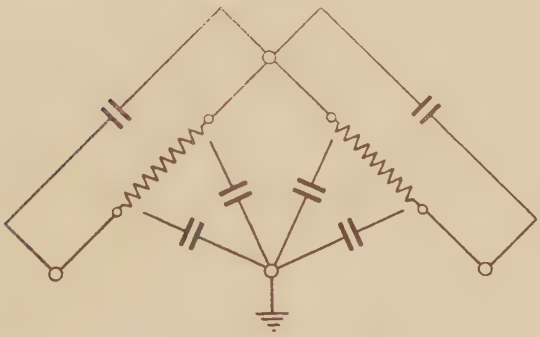
Thus, to secure a bridge ratio of $n : 1$, it is necessary to provide a coil whose windings have self inductances in the ratio $n^2 : 1$ and resistances in the ratio $n : 1$.

1.20. *Effect of Stray Capacities.*

One of the principal sources of error in bridges employing resistance ratio arms is that due to the shunting effect of stray capacities on the ratio arms.

These capacities may be either directly in shunt on either arm or they may be to other parts of the bridge or to earth, in which case they act indirectly across the arms.

Fig. 4.



Stray capacities in ratio arms.

The current shunted off through these capacities will be proportional to the e.m f. across them, which in the case of equal resistance ratio arms will be $\frac{1}{2}$RI, where R is the resistance of each arm, and I is the current into the bridge.

In the case of retardation coil ratio arms the effect of stray capacities may be examined by the aid of the transformed circuit shown in fig. 5, remembering that the point B′ is inaccessible and all capacities must act at the point B.

Putting in a capacity acting across the BC arm, fig. 6 is obtained.

Assuming that the coil gives an impedance ratio of $n : 1$, then the e.m.f. across the condenser C is

$$\begin{aligned} E &= -j\omega(n+1)IM + I\{R_2 + j\omega(L_2 + M)\} \\ &= -j\omega(n+1)InL_1 + I\{R_2 + j\omega(n^2L_1 + nL_1)\}. \end{aligned}$$

Since

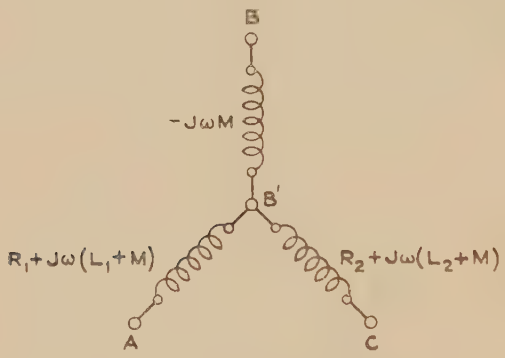
$$M = nL_1 \quad \text{and} \quad L_2 = n^2L_1.$$

Hence

$$E = IR_2.$$

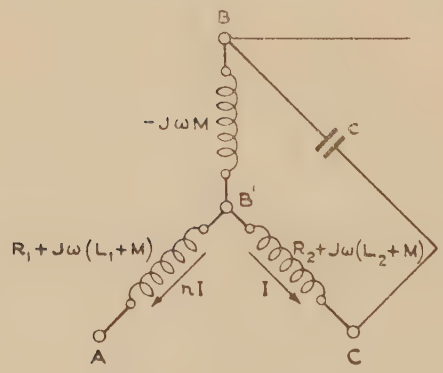
Thus the e.m.f. across the condenser, and consequently the magnitude of its shunting effect, depends on the D.C. resistance of the windings of the retard coil.

Fig. 5.



Transformed circuit for ratio arms.

Fig. 6.



Capacity shunting ratio arms.

1.21. *Effect of Leakage Coefficient* K.

To determine the effect of the leakage coefficient K in the case of a coil wound to give an unequal ratio, the following assumptions are made :—

(1) The coil consists of $(n+1)$ identical windings.

(2) The mutual inductance between any pair of sections is the same, and is KL_1, where L_1 is the inductance of any section.

This arrangement is as in fig. 7 *a*.

The equivalent star network may then be represented as is fig. 7 *b*.

Taking account of assumption (2) above, the value of L_2 is given by

$$nL_1\{1+(n-1)K\}.$$

Fig. 7 *a*.

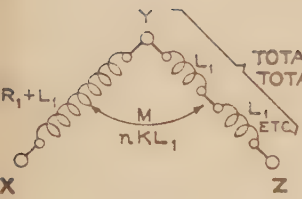


Fig. 7 *b*.

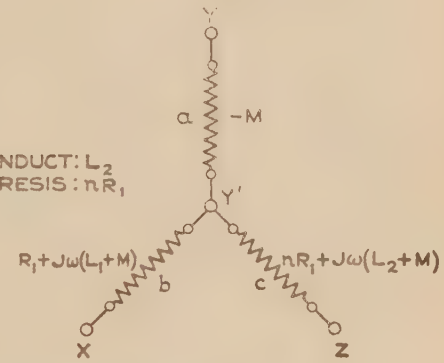


Fig. 7 *a*.—Network for unequal ratio arms.
Fig. 7 *b*.—Resolved network for unequal ratio arms.

Therefore the network is completely determined, the branch impedance being as below :—

$$(a) \quad -j\omega nKL_1,$$

$$(b) \quad R_1+j\omega L_1(1+nK),$$

$$(c) \quad nR_1+j\omega nL_1\{1+(n-1)K\}+j\omega nKL_1.$$

The ratio of the bridge-arm impedances, therefore, is

$$\frac{R_1+j\omega L_1(1+nK)}{nR_1+j\omega\{1+(n-1)K+K\}nL_1}$$

$$=\frac{R_1+j\omega L_1(1+nK)}{n\{R_1+j\omega L_1(1+nK)\}}$$

$$=\frac{1}{n}.$$

Therefore the leakage factor K does not introduce any error into the impedance ratio of the coil.

1.30. *The Unity Ratio Case.*

Referring to fig. 3, a unity ratio Wheatstone net may be obtained by writing $L_1 = L_2 = M$.

Errors may arise from two principal causes, namely, unbalances in the coil itself and capacities between the coil and the rest of the bridge circuit.

The errors in the coil itself may arise from unbalances in the self inductances in the halves of the winding, or from internal skew capacities affecting the symmetry of the winding.

The errors arising in the coil itself are complex in nature, and the following treatment deals only with the simplest factors.

In general it is sufficient to say that if these inherent unbalances in the coil are not small enough to neglect altogether—that is to say, if they cause the impedances of the two arms to differ by more than a few parts in a million—then some means would be necessary for their adjustment, and the resulting ratio arm assembly would have little advantage over resistive arms.

As a matter of interest it may be pointed out that an adjustment of retard coil ratio arms may be made by means of a resistance slide wire to balance the direct current resistance of the windings, and a variable condenser connected from the extremity of one of the arms to a point in the generator arm, which is connected to the mid-point of the retard coil through 500 ohms. This expedient is, however, not really practicable, and would introduce undesirable complications.

It may be assumed for the time being that coils may be so constructed that the inherent unbalance of the two halves is within the limits of 10 parts in a million. The direct current resistance unbalance of the windings can be reduced to 0·01 ohm, so that the errors due to this cause are negligible.

In this case the effect of external capacities may be determined at once. Referring to the fig. 3 above, and assuming a unity ratio bridge, the circuit conditions when a single external capacity exists can be shown, as in fig. 8.

Considering the bridge at the point of balance, the voltage across the condenser C is

$$-2I_1 j\omega L + (R + 2j\omega L)I_1 = V.$$

$$\therefore \qquad V = RI.$$

Also at balance, since A and C are at the same potential

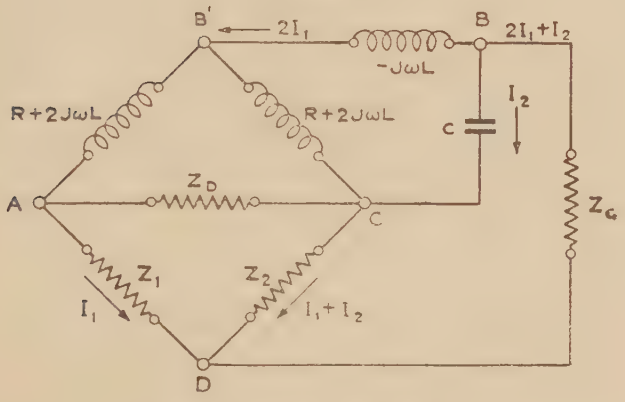
$$I_1 Z_1 = (I_2 + I_1) Z_2,$$

and hence

$$\frac{Z_1}{Z_2} = 1 + \frac{I_2}{I_1}$$

$$= 1 + \frac{V}{Z_c I_1},$$

Fig. 8.



Capacity shunting one ratio arm.

where Z_c is the impedance of the condenser

$$= 1 + \frac{j\omega CRI_1}{I_1}.$$

$$\therefore \quad \frac{Z_1}{Z_2} = 1 + j\omega CR$$

$$= 1 + jp \quad \text{(say)}.$$

If, then, values be assumed for Z_1 and Z_2, the percentage errors in measurement may be calculated by substitution in the equation arrived at above.

1.31. *Errors due to Capacity* C *Bridged Across One Ratio Arm.*

$$\frac{Z_1}{Z_2} = 1 + jp \quad \text{from above.}$$

Put

$$Z_1 = R_1 + jX_1,$$

$$Z_2 = R_2 + jX_2.$$

Then $$R_1 + jX_1 = R_2 + jX_2 + jpR_2 - pX_2.$$

$$\therefore \quad R_1 = R_2 - pX_2$$

and $$X_1 = X_2 + pR_2;$$

and writing Q for $\frac{X_2}{R_2}$,

$$R_1 = R_2(1 - pQ) \quad \text{and} \quad X_1 = X_2\left(1 + \frac{p}{Q}\right).$$

Substituting values for p and Q, the percentage errors in any particular case may be evaluated.

These figures may be used to show that the measurement of effective resistance is subject to greater errors when the time constant of the impedance is high, while the measurement of reactance is least accurate for impedances of low-phase angle. This, however, is not a fault particular to the type of bridge here described ; it is present in nearly all inductance measurements.

1.40. *The Unequal Ratio Case.*

Referring again to fig. 3, we have

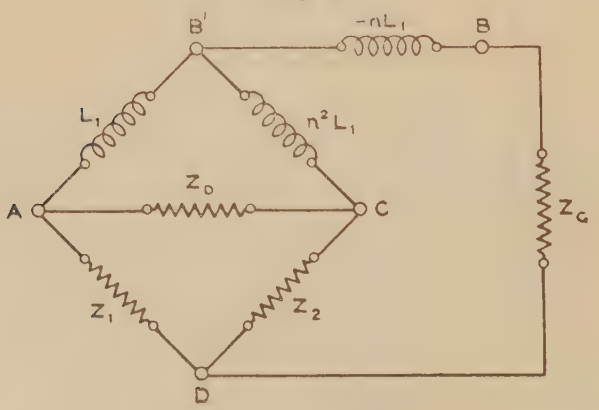
$$L_2 = n^2 L_1 \quad \text{and} \quad M = \sqrt{L_1 L_2} = nL_1.$$

It may also be arranged that

$$R_2 = nR_1;$$

then the equivalent bridge network without mutual inductance may be shown thus :—

Fig. 9.



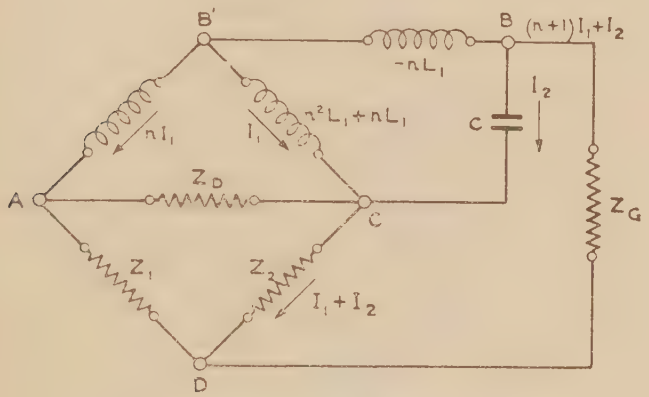
Equivalent bridge network.

The inductance of the two halves of the windings of the coil are in the ratio $n^2 : 1$. Therefore the number of turns on the two halves of the coil must be in the ratio $n : 1$—namely, the same ratio as that of the required bridge ratio.

1.41. *Errors due to Capacity Bridged Across One Ratio Arm.*

Assuming that the inherent unbalances in the coil do not appreciably affect the ratio, the effect of external capacities may be shown as follows :—

Fig. 10.



External capacities in unequal ratio arms.

The voltage across the condenser C is

$$-(n+1)nj\omega L_1 I_1 + nR_1 + n(n+1)j\omega L_1 I_1 = V.$$

$$\therefore \quad V = nR_1 I_1.$$

Also at balance the points A and C are at the same potential.

$$\therefore \quad nI_1 Z_1 = Z_2(I_1 + I_2).$$

$$\therefore \quad \frac{Z_1}{Z_2} = \frac{1}{n}\left(1 + \frac{I_2}{I_1}\right)$$

$$= \frac{1}{n} + \frac{I_2}{nI_1}.$$

$$\therefore \quad \frac{Z_1}{Z_2} = \frac{1}{n} + \frac{V}{Z_c n I_1} = \frac{1}{n} + \frac{n I_1 R_1}{Z_c n I_1}$$

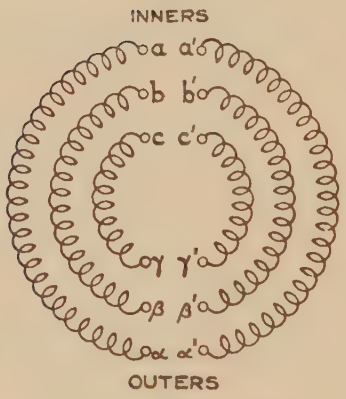
$$= \frac{1}{n} + \frac{R_1}{Z_c}$$

$$= \frac{1}{n}\left(1 + n\frac{R_1}{Z_c}\right)$$

$$= \frac{1}{n}(1 + n R_1 j\omega C)$$

$$= \frac{1}{n}(1 + jnp).$$

Fig. 11.



Multifilar windings.

It follows from the above that the errors calculated for the unity ratio cases will apply for the case of $n:1$ ratio when they are multiplied by n. That is,

$$R_1 = \frac{R_2}{n}(1 - pmQ),$$

$$X_1 = \frac{X_2}{n}\left(1 + \frac{pm}{Q}\right).$$

1.50. *Windings of a Retard Coil to give a* 2 : 1 *Ratio.*

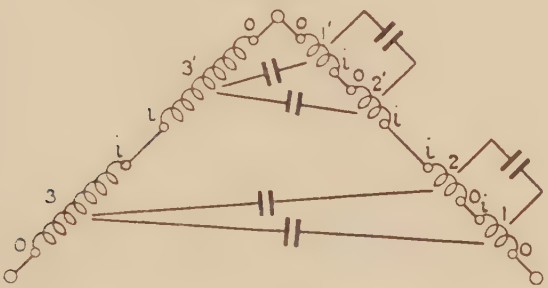
The distribution of the windings on a 2 : 1 ratio coil is indicated in fig. 11.

The winding consists of two sections of trifilar wire. The two possible methods of making the connexions are as below:—

1. Join c, c'; a, a'; b, b'; also α, β; γ, α';
   then the winding is divided in 2 : 1 ratio at the point γ, α'.

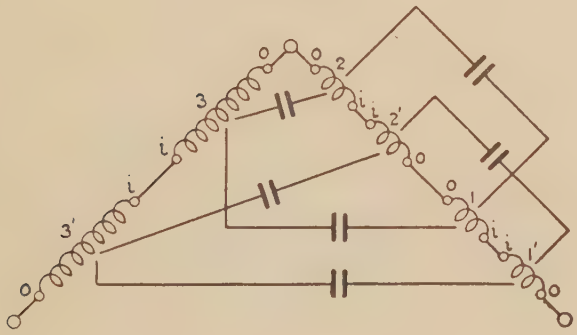
2. Join c, c'; α', α; a', β'; β, a; also b, b';
   then the winding is divided in 2 : 1 ratio at the point γ', α'.

Fig. 12.



Arrangement No. 1 for capacities of windings.

Fig. 13.



Arrangement No. 2. for capacities of windings.

The above diagrams show the distribution of the major capacities corresponding to the two possible methods of making the connexions in a 2 : 1 ratio coil wound with trifilar wire in two sections.

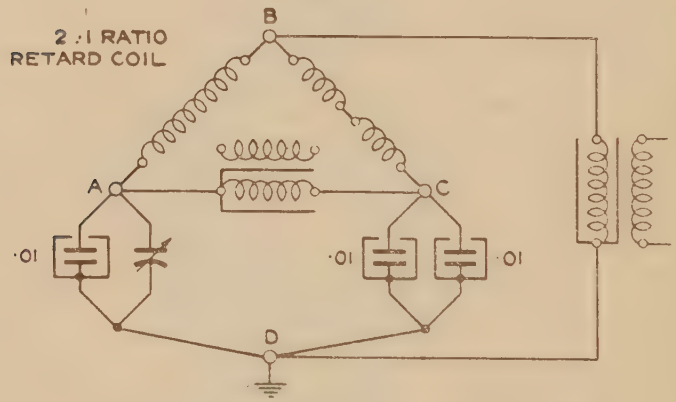
1.51. *Accuracy of* 2 : 1 *Ratio Coil.*

The exactness of the impedance ratio is checked in the following manner :—

A bridge is set up as shown in fig. 14, and the unbalances between each of the three fixed condensers and the other pair in parallel is measured on the air-condenser. If the ratio of the bridge arms is exactly 2 : 1, then the sum of these unbalances should be zero.

The error in the ratio can be determined from a consideration of the figures obtained from this test. In practice it is found that of the two arrangements of connexions mentioned above arrangement No. 1 is the better, and by using it a

Fig. 14.



Arrangement for checking the accuracy of 2 : 1 ratio arms.

2 : 1 ratio may be obtained which is accurate to about 1 in 1000.

It is realized that, owing to the multiplicity of windings and the unavoidable skewness of the capacities, the same accuracy cannot be expected from unequal ratios as from unity ratio coils ; but since for all the most precise work a unity ratio bridge would be used, this is not of great importance.

1.60. *Shielding* *.

The construction of the coil does not allow the ratio arms to be shielded from one another, as is usual in shielded bridges, and instead the ratio arms form a single unit in a common shield.

* G. A. Campbell, "The Shielded Balance," 'Electrical World' (1904).

The rest of the shielding of a bridge circuit is also affected and generally simplified by the presence of the retard coil ratio arms in consequence of their property of suppressing the effect of capacities shunted across them.

The detailed treatment of the retard coil, both in its design and its relation to the shielding of the bridge, depends on the particular purpose for which it is intended.

Certain typical cases will therefore be discussed in some detail.

2. Application.

2.10. *Impedance Bridges.*

The coil to be used for impedance bridges will depend on the nature of the impedances to be measured and the frequency at which the bridge is to be used.

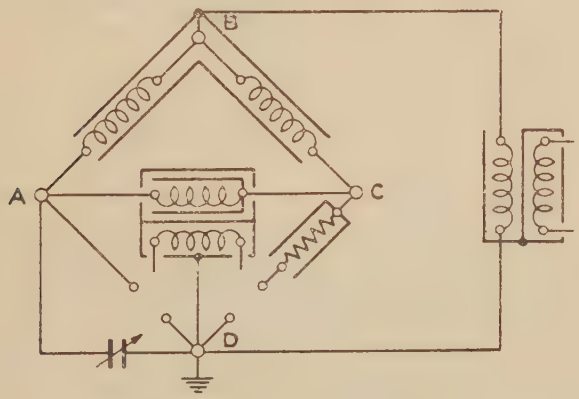
Referring to paragraph 1.11 the equivalent series impedance of the windings of the retard coil in the bridge network is

$$R_1+R_2+j\omega(L_1+L_2+2M),$$

and this should be made approximately double the mean value of the impedance to be measured, provided this is not small compared with the impedance of the detector.

2.11. A suitable shielding scheme* for such a bridge is shown below if the measurements may be made with one end of the unknown to earth.

Fig. 15.



Shielded impedance bridge.

* An account of a complete shielding scheme for an impedance bridge will be found in a paper by M. G. Fergusson, "Shielded Impedance Bridge," 'Bell Technical Journal,' vi. p. 142 (1927).

2.12. Such a bridge may be constructed so that the capacity unbalance across the ratio arms does not exceed 1000 mmf.

Referring to paragraph 1.31, we may now assume the following values:—

$$C = 1000 \text{ mmf.},$$

$$R = 10\omega \times 10 \text{ ohms},$$

$$\omega = 10{,}000,$$

$$\frac{X_2}{R_2} = 200,$$

then the error in resistance reading due to the capacity C is

$$100pQ \text{ per cent.}$$

$$= 100\omega CR\frac{X_2}{R_2} \text{ per cent.}$$

$$= 100 \times 10{,}000 \times 1000 \times 10^{-12} \times 10 \times 200$$

$$= 2 \text{ per cent.},$$

and the error in reactance reading

$$= 100\frac{p}{Q} \text{ per cent.}$$

$$= 5 \times 10^{-5} \text{ per cent.}$$

The above would correspond to the measurement of a high-phase angle inductance coil. If, on the other hand, a value of Q=1 were taken, the errors would be

$$\text{Error in } R_2 = 0{\cdot}01 \text{ per cent.},$$

$$\text{Error in } X_2 = 0{\cdot}01 \text{ per cent.}$$

2.20. *Capacity Bridges.*

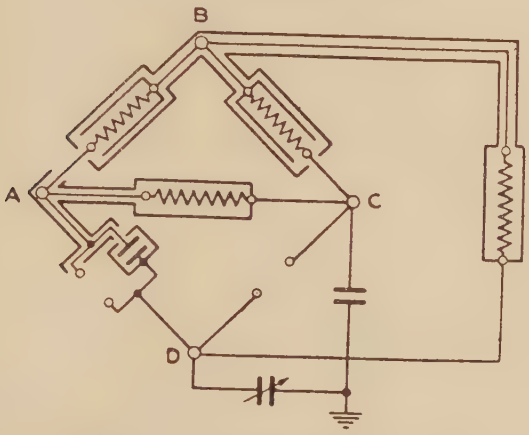
The shielding of a type of equal ratio comparison bridge for the measurement of capacity is shown below (omitting the earthing screen) when resistance ratio arms are used.

The shielding of the AD and CD arms is comparatively simple in the case of a capacity bridge, and a suitable arrangement with retard coil ratio arms is shown in fig. 17.

Such a bridge, in addition to making accurate measurements of mutual capacity in the usual way, may be used for measurements of direct capacity in a manner which requires one reading only to be taken.

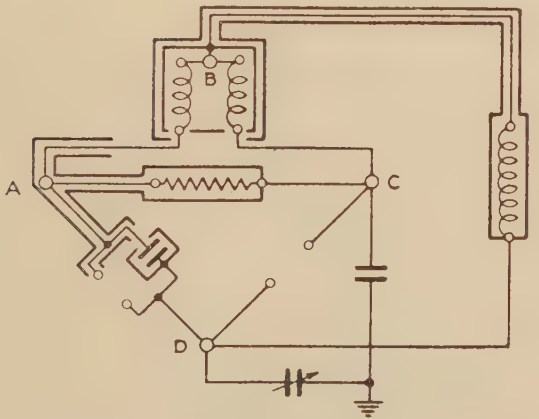
For example, in the case of a three-terminal system, as in fig. 18, if it is required to measure the direct capacity C_{bc}, the conductors A, B, and C would be connected respectively to the B, C, and D corners of the bridge (see fig. 16), so that

Fig. 16.



Shielded bridge with resistance ratio arms.

Fig. 17.



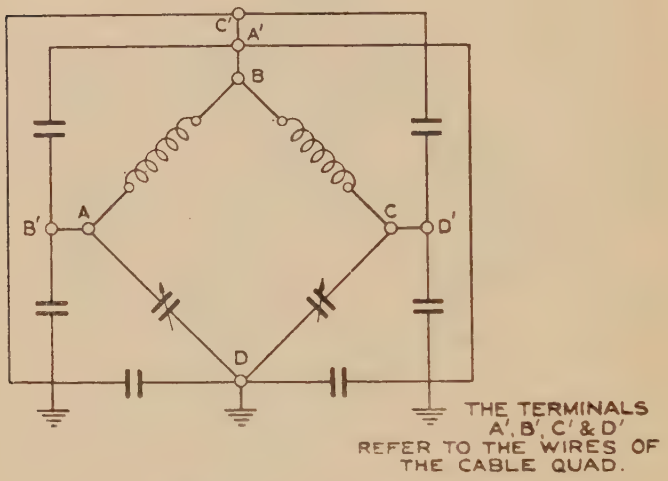
Shielded bridge with mutually inductive ratio arms.

the capacity C_{ab} is shunted by the ratio arms, and the capacity C_{ac} is across a diagonal of the bridge.

This method gives very good results provided that C_{bc} is

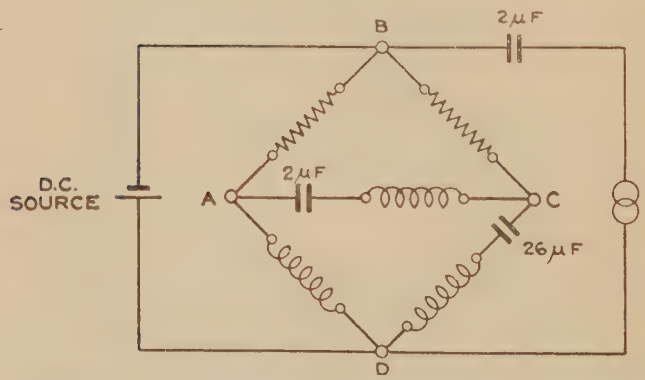
not small compared with C_{ab} and that it is not required to find the conductance of C_{bc}, since in the latter case errors of upwards of 10 per cent. will often be found.

Fig. 18.



Measurement of direct capacity.

Fig. 19.



Bridge for alternating current measurements with superimposed direct current.

2.30. It is sometimes necessary to use superimposed direct current while making A C. measurements, as in the bridge circuit shown in fig. 19.

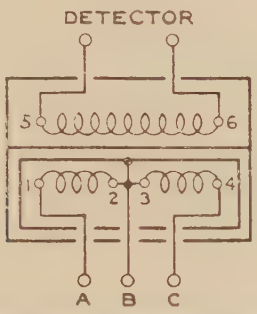
In this case there is difficulty in securing large values of direct current in the impedance tested if the usual 1000 ohm ratio arms are used on the A.C. bridge. This provides another example of the use of retardation coils, as they would very materially increase the efficiency of such a bridge from the D.C. point of view, the power loss being about 1/100 of that encountered when ratio arms of 1000 ohms are used.

2.40. *Incorporation of a Detector Winding.*

An alternative form of inductive winding used as ratio arms exists in the form of the "hybrid coil" or three winding transformer.

This type of coil can be used to provide the input winding and the ratio arms.

Fig. 20.



Incorporated detector winding.

It is possible to apply the type of winding described in this paper to improve the balance obtained on such a coil.

Similarly, a detector winding may be added to the usual windings described in the preceding pages, thus avoiding the necessity for an output transformer to the bridge. In this case the detector winding would be separated from the ratio arm windings by a complete electrostatic screen. The success of this arrangement depends on the completeness of this screen, and in any case such additional windings tend to disturb the exact balance obtained with the bifilar windings alone. This arrangement is shown in fig. 20, above.

3. *Résumé* of Principle and Advantages.

The essential points in the production of retard coil ratio arms are the use of a toroidal core and multifilar windings. The material of the core should have high permeability, in

order that the direct current resistance of the windings may be as low as possible.

The advantages of the use of these coils may be summarized.

The ratio arms assembly can be made a compact unit which easily fits into any shielding scheme ; moreover, the use of retard coil ratio arms often simplifies the shielding.

By correct design of the coil, the sensitivity of the bridge can be made higher than with resistance ratio arms when the sensitivity depends on the current which can be drawn from a given generator.

When the current through the unknown impedance is specified, the sensitivity is approximately the same as with resistive ratio arms.

The measurement of impedances at frequencies between 5,000 and 20,000 is rendered much easier, as the effect of small capacities, which is so great with resistive ratio arms, is reduced by the use of retardation coils.

Retardation coil ratio arms are very stable, since their balance is not affected by temperature effects, and it has been found that they can be more safely relied on than the best resistance ratio arms ; they are, too, more easily constructed when high quality ratio arms are required, and the cost is probably less when the degree of balance required is better than 1 in 1000.

Most of the coils made up so far for experimental purposes have been wound on a silicon steel core, although a successful experiment was made with iron dust in the case of a coil for a carrier frequency bridge. The high permeability of permalloy suggests that this material would be excellent as a core material for high quality retardation coil ratio arms.

The advantages of permalloy as a core material would lie in the ability to secure a sufficiently high inductance with low D.C. resistance, and in the very good value of the coupling factor obtained on such a core.

In conclusion, while the adaptation of such coils to precision apparatus is still in the experimental stage, it is believed that they will find a wide application in high frequency alternating current measurements.

The author wishes to express his indebtedness to the International Standard Electric Corporation for permission to publish this paper.

V. *The Influence of Chemical State on Critical X-Ray Absorption Frequencies. By* Prof. H. R. Robinson, *F.R.S., and* C. L. Young, *B.Sc.**

ALTHOUGH X-ray spectral terms are dependent mainly on nuclear charge, it has been known for some years that they are slightly displaced by changes in the state of chemical combination of the atom. The smallness of the effect is sufficiently well indicated by the length of time which elapsed before its discovery. It was first observed for X-ray absorption edges in 1920, and for emission lines in 1924. There is now an extensive literature of experimental work on this subject, much of which has been summarized in Siegbahn's 'Spectroscopy of X-rays' and in Lindh's 'Report' †. Finally, Aoyama, Kimura, and Nishina have succeeded in accounting quantitatively for the magnitudes of the displacements in certain cases ‡.

In view of well-known difficulties—particularly in connexion with the complex fine structure of absorption edges, which is still far from completely understood—it is desirable that the problem should be attacked from as many sides as possible. It is clearly one which lends itself to experimental investigation by the magnetic spectroscopy of the photoelectrons ejected from an element and its compounds by a primary X-radiation of suitable frequency. The details of this method, as applied to the determination of X-ray energy levels, are given fully in an earlier paper §.

Briefly, the element or compound under examination is made the "target" of a bombardment by homogeneous X-radiation. Pencils of the resulting secondary cathode rays are defined by a suitable slit system, and guided and focussed by a uniform magnetic field in such a manner that they produce accurately measurable traces on a photographic plate. The measurements lead to the value

* Communicated by the Authors.

† Lindh, *Phys. Zeitschr.* xxviii. p. 92 (1927).

‡ Aoyama, Kimura, and Nishina, *Zeitschr. f. Physik*, xliv. p. 810 (1927).

§ Robinson, Proc. Roy. Soc. A, civ. p. 455 (1923).

of the product rH, where H is the magnetic field strength and r the radius of curvature of the path of the electron, which is arranged to be perpendicular to H. From rH the kinetic energy W of the electron may readily be deduced; for small velocities it is given very nearly by $k(r\mathrm{H})^2$, where k is a constant which is known in terms of fundamental atomic constants. Then if ν_0 is the frequency of the primary X-radiation, and ν_a the critical absorption frequency of the atomic level under investigation, we have $\nu_a=\nu_0-k(r\mathrm{H})^2/h$, or $\nu_a=\nu_0-\mathrm{A}(r\mathrm{H})^2$ where A is another known constant.

If $\nu_a+\Delta\nu_a$ is the frequency of a neighbouring level, and $r-\Delta r$ the corresponding value of r, we have

$$\Delta r = \frac{\Delta\nu_a}{2\mathrm{A}\mathrm{H}^2 r} = \frac{r\Delta\nu_a}{2(\nu_0-\nu_a)}. \quad . \quad . \quad . \quad (1)$$

In comparing two neighbouring levels, we have to measure accurately the distance between the corresponding lines on the photographic plate; with our apparatus this distance is almost exactly $2\Delta r$. $\Delta r/\Delta\nu_a$ may therefore be taken as a measure of the "dispersion." If $\Delta\nu_a$ is the displacement produced in a given level by a change in the chemical state of the atom, $\Delta\nu_a$ is always small—of the order 1 Rydberg unit, or less. High dispersion is therefore essential.

There are obvious practical objections against increasing r above 5–10 cm. If $\nu_0-\nu_a$ is made very small, another practical difficulty arises, as a result of the rapid falling off of the photographic efficiency of slow electrons with diminishing velocity. Theoretically the practical difficulties may be overcome, and the dispersion increased almost indefinitely, by introducing a suitable combination of retarding and accelerating fields along the trajectories of the electrons. This plan, however, has the not uncommon defect of being simpler in conception than in execution.

In 1926 one of us, with Mr. A. M. Cassie, applied the method of magnetic spectroscopy to the problem of these displacements produced by change in chemical state, using a fairly soft primary radiation (copper Kα). There are, however, other difficulties, besides those directly due to the low photographic efficiency of the electrons, in the

* *Cf.* Ledrus, *Comptes Rendus*, clxxvi. p. 383 (1923).

investigation of regions of the photographic plate corresponding to small values of $\nu_0 - \nu_a$. These are principally difficulties arising from the continuous background of scattered and straggled electrons, and from the ease with which slow electrons are diffused by irregularities in the target surface. For these reasons, although the experiments of 1926 were sufficiently good to show the displacements in question, it was not possible to obtain photographs which could be measured with sufficient accuracy to warrant publication.

We have recently, in the course of other work, been able to develop a satisfactory technique for slower electrons than those previously recorded, and to measure the displacements with much greater accuracy. Using copper $K\alpha_1$ as primary X-radiation (frequency = 592·8 Rydberg units (ν R)), we have been able to measure the difference between the K level of chromium in the metallic state and as hydroxide. This involves the photography of electrons with energies just under 2000 electron-volts—which we have so far found to be near the practical limit at which we can work without excessively long exposures and without resorting to the use of Schumann plates.

According to the measurements of Lindh *, the level values are :—

Chromium, element, K edge, $\nu/R = 440{\cdot}99$.

$Cr(OH)_3$,, K edge, $\nu/R = 441{\cdot}95$.

Taking 5 cm. as radius of curvature of the paths of the secondary cathode rays, and assuming that the same values of ν R are applicable in our experiments, this difference would correspond to a shift of just over 0·03 cm. on the photographic plate (Eqn. 1 above). This is not large, but it is many times greater than our errors of measurement on a good line, and would not be difficult to detect in the normal course of our experiments.

In order to make the test as rigorous as possible, we modified the experimental procedure in such a way as to eliminate possible errors in setting the photographic plate or in measuring the absolute distances of the lines from the fiducial line. The K lines of $Cr(OH)_3$ and metallic

* Lindh, *Zeitschr. f. Physik*, xxxi. p. 210 (1925).

chromium were photographed on the same plate in successive exposures, the plate being kept fixed in the plate-holder while the target was changed, and different halves of the plate being exposed in the two cases. The normal and displaced K lines are thus obtained in positions which enable the displacement to be measured with the greatest possible accuracy, and with no possibility even of minor errors which might conceivably occur through minute shrinkage or expansion of the photographic emulsion during manipulation. In controlling experiments it was shown, by reversing the order of the portions of the photographic plates used to record the lines of the element and the hydroxide respectively, that there was no sensible error due to any possible lack of symmetry in the apparatus.

The result of the measurements on metallic chromium is :—$r\mathrm{H}=153{\cdot}2$ cm. gauss ; equivalent ν/R calculated 153·0 Rydberg units. Hence K critical frequency for metallic chromium $=(592{\cdot}8-153{\cdot}0)=439{\cdot}8$ Rydberg units, in good agreement with Lindh's value. These two values are not strictly comparable, as the calculation involves fundamental atomic constants which are not known with sufficient accuracy. For this reason, we have not attempted to measure the absolute energy of the line with any very high accuracy. The difference between this and the line for $Cr(OH)_3$ has, however, been measured with great care. Errors in the fundamental constants and systematic errors in our measurements do not appreciably vitiate the values obtained for small differences of this kind.

We find, as the mean of measurements on a number of plates, obtained with different magnetic fields, that the K line of $Cr(OH)_3$ is displaced, relative to that of the element, in the sense indicated by the X-ray spectroscopic results. In other words, the secondary cathode rays emerge from the K level of the chromium atom in the compound with appreciably smaller velocities than those from the K level of the element. This in itself is very satisfactory in view of recent evidence of the extreme complexity of the absorption edges even of elements. We find, however, instead of Lindh's difference of 0·96 Rydberg unit, about half this value. In round figures, the mean of our measurements gives $\Delta\nu_a/\mathrm{R}=0{\cdot}5$ Rydberg unit with a probable error—fairly generously estimated—of

$\pm 0{\cdot}15$ unit. It is therefore practically certain that the displacement as measured by corpuscular spectrometry is appreciably less than that obtained by Lindh with the X-ray spectrometer. Further work on this is desirable, as such a difference, if it is real, must be significant.

We cannot, of course, be quite certain that our chromium hydroxide target remained unchanged throughout an exposure; it seems at least possible that the surface layers, which alone are effective, become dehydrated during an intense X-ray bombardment *in vacuo*. Lindh's results do not include a value for the K edge of chromium in Cr_2O_3. In an earlier paper Coster * has given a value for the oxide, but no measurement for the element, so no data are available for the direct comparison of the levels. So far as can be judged from a comparison of results which are common to Lindh and Coster, there is not likely to be a large difference between the K levels in the oxide and the hydroxide respectively. Dehydration therefore does not appear to afford a plausible explanation of the discrepancy.

We have two photographs, taken with relatively large magnetic fields, which also show the "fluorescent" corpuscular lines, due to the internal conversion of the K energy of the excited chromium atoms. The effects here are more complicated, as more than one level is involved, but there is definite evidence of displacements of the fluorescent lines in compounds. The displacements are of the same order of magnitude as those of the secondary cathode rays, but we have not yet made sufficiently accurate measurements to enable us to communicate any definite results in these regions.

Much of the material used in this work was purchased by means of a grant from the Government Grant Committee of the Royal Society, for which we desire to make acknowledgment. The metallic chromium used was in the form of a thin plating on copper, for which we are indebted to the Research Department of the Metropolitan-Vickers Electrical Company.

* Coster, *Zeitschr. f. Physik*, xxv. p. 83 (1924).

VI. *Studies in Coordination.* Part I.—*Ion Hydrates. A Correction.* *By* F. J. Garrick, *B.A.**

IN the author's paper under the above title (Phil. Mag. ix. p. 131, 1930) one of the equations used is incorrect. This is equation (7), p. 139, and should read as follows:—

$$F_E = p \cdot \frac{\partial E}{\partial r} = -\frac{2zep}{r^3} + \sum_{k=1}^{k=(n-1)} p^2/s_k^4 \cdot 3(1+\cos^2\theta)\cos\theta.$$

Table I.

Ion.	n.	r.	$-\phi_E$.	$-\phi_{R_1}$.	$-\phi_{R_2}$.	$-\phi$.
Na^+	4	2·05	132	27	1	104
	6	2·19	138	21	3	114
	8	2·44	120	9	9	102
K^+	6	2·54	106	21	1	84
	8	2·73	101	15	3	83
Rb^+	6	2·67	96	20	0	76
	8	2·84	95	15	2	78
Cs^+	6	2·88	83	16	0	67
	8	3·02	85	13	1	71
	12	3·34	77	7	23	47
Mg^{2+}	4	1·64	631	141	9	481
	6	1·78	606	93	26	487
	8	2·03	494	34	54	406
Ca^{2+}	6	2·05	454	99	6	349
	8	2·23	417	62	21	334
Sr^{2+}	6	2·17	402	92	4	306
	8	2·33	385	65	13	307
Ba^{2+}	6	2·37	332	66	1	265
	8	2·49	339	43	7	289
	12	2·73	326	35	174	117

The effect of the error is small; most of the values for r in Table III. of the paper are slightly too large, but the values of $-\phi$ are for the most part nearly correct. The present note gives the revised results (Table I.).

It will be seen that the conclusions reached in the former paper hold good in every case except that of Rb^+, for which

* Communicated by the Author.

it now appears that the coordination number is definitely 8, in agreement with Sidgwick's Rule. The agreement between this rule and the theory is now complete, as shown.

Ion.	Coord. No. (found).	Coord. No. (Sidgwick Rule).
Na, K, Mg, Ca	6	6
Rb, Cs, Sr, Ba	8	8

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VII. *Studies in Coordination.* Part II.—*Ion Ammoniates.*

By F. J. Garrick, *B.A.**

IN previous papers † it was shown that the electrostatic theory of coordination as there developed led to coordination numbers for ion hydrates in agreement with the general covalency rule of Sidgwick. In the present paper this theory is extended to ammino-compounds. The necessary data are as follows :—

1. *Force Constants.*

Rankine and Smith ‡ give for NH_3 and Ne $\pi\omega^2=0{\cdot}640$ and $0{\cdot}417$ respectively. This, with the assumptions made in paper I., gives

$$\frac{\sigma^{(\nu)}_{NH_3}}{\sigma^{(\nu)}_{NQ}}=1{\cdot}24.$$

From this, with the generalized diameters of Ne and various ions as given in paper I., the force constants are derived in the usual way.

* Communicated by the Author.

† Garrick, Phil. Mag. (Jan. 1930); see also the correction published later (*suprà*, p. 76). These two papers will be referred to as I. and I. (*a*) respectively.

‡ Rankine and Smith, Phil. Mag. xlii. p. 601 (1921).

2. *Electrical Constants.*

The permanent dipole moment (P) of the ammonia molecule is given by Jona* as $1{\cdot}44 \times 10^{-18}$ E.S.U. The deformability (α) is obtained from the index of refraction of ammonia gas for visible frequencies (Landolt-Börnstein) by the relation

$$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \frac{4}{3}\pi N\alpha,$$

and is found to be $2{\cdot}21 \times 10^{-24}$. Using these data, the calculation is carried out exactly as described in the previous papers. The results are shown in the Table, where the symbols have the same significance as before :—

Ion.	n.	r.	$-\phi_E$.	ϕ_{R_1}.	ϕ_{R_2}.	$-\phi$.
Na^+	4	2·26	105	23	1	81
	6	2·41	111	18	3	90
	8	2·69	97	8	8	81
K^+	6	2·70	89	18	1	70
	8	2·91	85	13	4	68
Rb^+	6	2·83	81	17	1	63
	8	3·02	80	13	3	64
Cs^+	6	3·04	70	14	0	56
	8	3·19	72	12	1	59
	12	3·52	68	7	4	57
Mg^{2+}	4	1·73	607	141	10	456
	6	1·91	543	79	32	434
	8	2·22	420	23	56	341
Ca^{2+}	4	2·02	411	115	2	294
	6	2·17	415	90	9	316
	8	2·39	365	51	27	287
Sr^{2+}	6	2·28	371	88	5	278
	8	2·48	340	55	18	267
Ba^{2+}	6	2·48	306	70	2	234
	8	2·63	301	52	10	239
	12	2·93	279	26	22	231

From the Table the favoured coordination numbers are found to be as follows :—Mg^{2+}, 4 ; Na^+, K^+, Ca^{2+}, and Sr^{2+}, 6 ; Rb^+, Cs^+, and Ba^{2+}, 8. These numbers agree with the coordination numbers of the elements according to Sidgwick's Rule with two exceptions, namely Mg^{2+} and

* Jona, *Phys. Zeits.* xx. p. 14 (1919).

Sr^{2+}, whose coordination numbers are 6 and 8 respectively. A direct appeal to observation is useless ; in solution the ammines of these ions are too much dissociated for their formulæ to be determined, while in dealing with solid ammines it is necessary to know their crystal structure. Even where it can be shown that the crystalline ammine has an ion lattice with all the ammonia present as a complex cation, the results of the present theory would not be rigidly applicable, because the ammonia molecules will be polarized differently, since the electric field to which they are subjected in the lattice is not simply that of the central ion of the complex. According to the work of Biltz and his collaborators * the magnesium halides form no definite ammines higher than the diamine ; further addition of ammonia leads to mixed crystal formation, while both calcium and strontium halides form octammines and barium a decammine. These have very different properties from the stable hexammines like $NiCl_2 . 6NH_3$, which are known to have a lattice of the CaF_2 type in which the positive ion is a complex cation, say $[Ni(NH_3)_6]^{2+}$.

Ammines in Solution.

Comparing the values for $-\phi$ given in the Table with those given for hydrates in I. (*a*), it will be seen that the latter are always the greater, implying that in solution the ammines should be unstable and form hydrates. This is in agreement with observation for the elements considered. But since ammonia, while having a smaller permanent moment than water, has a greater polarizability, it is clear that, with increasing charge and decreasing size of the central ion, $-\phi$ for the ammine must increase more rapidly than $-\phi$ for the hydrate. Thus the ratio $\frac{\phi \text{ Ammine}}{\phi \text{ Hydrate}}$ expressed as a percentage varies from 79 to 83 per cent. for the alkali metals, while for the smaller divalent ions, Mg^{2+}, Ca^{2+}, and Sr^{+2}, it is between 93 and 95 per cent. This corresponds to the fact that in ammoniacal solutions of salts of Ca, etc , some slight ammine formation appears to take place ; in solutions of alkali metal salts there is no trace of ammine formation. The force constants of trivalent ions are unknown, so that the theory cannot be applied to them ; but it is clear that the ratio $\frac{\phi \text{ Ammine}}{\phi \text{ Hydrate}}$ will be still

* Biltz, *Zeits. für Anorg. Chem.* cxxx. p. 93 (1923).

greater in this case and may even be greater than unity, so that trivalent ions should form ammines fairly stable in solution were it not that in most cases the ion only exists in acid solution, being removed from neutral or alkaline solutions either by the precipitation of a very insoluble hydroxide (*e. g.* Al^{3+}, Fe^{3+}) or by the formation of a complex anion (AlO_2^-). But it seems quite plausible to explain the stable ammines of Cr^{3+} and Co^{3+} on the electrostatic basis.

In addition to the ammines of trivalent ions, there is another group of ammines more or less stable in solution. These are ammines in which the coordination number is less than the usual, which do not correspond to the solid ammine in formula, and in which the central ion is not of inert-gas type. Thus Ag and Cu halides in the solid state form sesqui- or tri-ammines, which according to Biltz (*loc. cit.*) are to be regarded as molecule-ammines. In solution, however, they form stable diamines. Again, a number of divalent elements like Cu, Ni, Zn form solid hexammine salts, as would be expected, but their ammines in solution are tetrammines. To account for their formation and stability it may be supposed that they are really hydrato-ammines—tetrammine-dihydrates for the divalent ions and diammine-tetrahydrates for the univalent ions. Such mixed compounds would normally have $-\phi$ values intermediate between those for hexammine and hexahydrate, so that one or other of these would be the most stable form. But a mixed complex of unsymmetrical space structure would exert a resultant electric field at the central ion due to the different dipole moments of the two kinds of molecule. ϕ_E would then include an additional term due to the polarization of the central ion, and if the latter were sufficiently polarizable the additional term could be of sufficient magnitude to make the mixed compound more stable than either hexammine or hexahydrate. Now the ions in the transitional periods, which have incomplete or "18" shells, are much more polarizable than the corresponding ions of inert-gas type (see, *e. g.*, the refractivity data of Fajans and Joos*), and it is precisely these ions which form the abnormal ammino-ions of the type under consideration.

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* Fajans and Joos, *Zeits. für Physik*, xxiii. p. 1 (1924).

VIII. *Newton's Law of Gravitation in an Infinite Euclidean Space.* By John Dougall, *M.A., D.Sc., F.R.S.E.**

Introduction.

It appears to be at present a generally accepted belief among physicists and astronomers that an infinite Euclidean spatial world, in which the average density of matter over a large region has approximately the same value everywhere, and in which Newton's Law of Gravitation holds universally, cannot be regarded as a possibility, being inconsistent with the observed finiteness of interstellar gravitational fields.

The following paper contains a criticism of the grounds on which this belief is founded, leading to a conclusion definitely adverse to the prevailing view.

The point on which the whole question turns is the fact that Newton's Law, as ordinarily stated, is ambiguous unless the field considered is finite. If we are dealing with infinite space, the law must in general be supplemented by some convention or definition, analogous to the specification of the order of the terms in a conditionally convergent series which is to be summed.

The definition adopted in the present paper is so simple and natural as to seem almost inevitable. But it is not the definition assumed, or rather implied, in the ordinary theory, and the results to which it leads differ sufficiently from those usually obtained to affect very materially the decision on the question at issue. It is shown, in fact, on the basis of the new definition, that it is perfectly consistent with the Newtonian law of the inverse square of the distance for matter to be distributed in an infinite Euclidean space in such a way that :—

(*a*) the average density of the matter within any very large spherical volume is approximately constant, though the density itself may vary within wide limits, while nevertheless

(*b*) the gravitational intensity at every point of space is finite, and

(*c*) the difference of potential between any two points whatever is likewise finite, *i. e.*, less than an assignable number independent of the choice of points.

* Communicated by the Author.

A considerable part of the paper is taken up with the determination of a set of conditions which, if satisfied by the distribution of matter, are sufficient to ensure the results just mentioned. Subject to these conditions, it is found that Poisson's equation

$$\nabla^2 V = 4\pi\rho$$

connecting the potential V with the density ρ of matter assumes the modified form

$$\nabla^2 V = 4\pi(\rho - \bar{\rho}),$$

where ρ is the constant average density—that is to say, the limit, for p tending to infinity, of the quotient of the mass within any sphere of radius p, and fixed centre, by the volume of the sphere.

No conditions to be satisfied at infinity by the potential V are required. These are replaced by the condition that V is everywhere finite. It is well known that this condition, combined with the differential equation and the usual suppositions as to continuity, *defines* V, in the sense that if one solution exists, any other can only differ from it by a constant.

The modification of Poisson's equation suggests—and indeed, if it is accepted, almost necessitates—a corresponding modification of the equations of General Relativity. The change would have quite inappreciable effects in all the ordinary applications, but—so far, at least, as a first approximation is concerned—it would remove an outstanding difficulty with respect to the behaviour of the Einsteinian potentials at infinity and thus, incidentally, detract materially from the plausibility of the current theory of the finiteness of space.

Newton's Law and Infinite Space—Einstein's View.

§ 1. The purpose for which Newton's Law is used is to define the force acting on a hypothetical particle of unit mass placed at any assigned point of the field. In practical applications to the astronomy of the solar system it is always assumed that the only attracting masses which need be taken into account are the masses belonging to the system itself, the total effect due to external masses being considered negligible; and the assumption appears to be abundantly justified by results.

Does the success of this hypothesis allow us to draw any conclusions regarding the distribution of matter in space as a whole? Is the stellar universe "a finite island in the

infinite ocean of space *," or should we believe rather that "however far we might travel through space we should find everywhere an attenuated swarm of fixed stars of approximately the same kind and density"?

These questions have attracted much attention within recent years on account of their bearing on the General Theory of Relativity.

Thus Einstein †, following Seeliger, came to the conclusion—but on grounds which we are going to try to prove inadequate—that an infinite Euclidean space in which Newton's Law holds throughout, and in which the average density of matter is everywhere broadly the same, is definitely incompatible with the finiteness of gravitational forces and potential differences in space, as attested by the finiteness and even comparative smallness of the relative velocities of the stars. He turned therefore to the "finite island" theory but, finding it impossible to make his potentials satisfy the conditions at infinity which this theory seems to impose, he finally cut the knot by introducing into the gravitational equations a "cosmological term" that allowed him to abolish the infinitude of space altogether.

Weyl ‡ accepts the view that space is finite, but not quite on the same grounds as Einstein. His objection to the infinitude of space would lose its force altogether if Poisson's equation were modified as suggested above.

§ 2. In coming to their decision about Newton's Law, Einstein and Weyl rely upon the supposed fact that the law of the inverse square carries with it as a consequence Poisson's equation, or the practically equivalent proposition known as Gauss's Theorem. Einstein's argument is in effect as follows §: by Gauss's Theorem, the average normal attraction over the surface of a sphere $= 4\pi$ (Mass within sphere ÷ area of surface). On the supposition of a finite average density of matter, the mean intensity at the surface would therefore obviously become infinite with the radius of the sphere, which is contrary to observation, so that Newton's Law cannot hold in a roughly uniform world.

* A. Einstein, 'Relativity: the Special and the General Theory' (translated by R. W. Lawson), chap. xxx.

† A. Einstein, 'Kosmologische Betrachtungen . . .,' *Sitzungsber. d. Pr. Ak. d. Wiss.* (1917) (translated in the 'Principle of Relativity' by W. Perrett and G. B. Jeffery).

‡ H. Weyl, 'Space—Time—Matter' (translation by H. L. Brose), pp. 275-279.

§ A. Einstein, 'Relativity: the Special and the General Theory,' p. 106.

On the premises assumed, the conclusion indubitably follows. What we question is the correctness of Gauss's Theorem, for an infinite field. But before the nature of the objection can be explained, it is necessary to go back to first principles and examine what Newton's Law, in this general case, really means.

Definition Supplementary to Newton's Law.

§ 3. It is implied in Newton's Law that the effects of the various masses in the field on the intensity at a given point are *additive*, so that the rectangular components of the intensity are to be found by algebraic summation (or integration) of the components due to the separate masses. No difficulty arises in the summation process so long as the total volume occupied by the masses is finite; but the same cannot be said when they extend to an infinite distance, for the series which gives any component contains both positive and negative terms, and the sum of the terms of either type is in general infinite.

To see this we need only consider the simple case of a spherical shell of uniform density. The intensity at the centre due to either of two hemispheres into which the shell may be imagined to be divided is a constant multiple of the thickness of the shell, and therefore becomes infinite when the outer radius is indefinitely increased. Nevertheless the intensity at the centre (and indeed at any point in the hollow of the shell) is rigorously *nil*. There is, as it were, an interference effect between the fields due to the two shells taken separately.

Hence, before we can begin to speak at all about the intensity of field due to a distribution of masses extending to infinity, it is absolutely essential to *define the order* in which the masses are to be taken when we are calculating the component intensities at an assigned point by summation of the effects of individual masses. The natural and obvious course is—to speak somewhat vaguely for the moment—to take the masses in the order of their nearness. We therefore give the following:—

Definition A: *The gravitational intensity at a point* P *in a field containing masses extending to infinity is to be found by calculating by Newton's Law the intensity due to the matter contained within a sphere of radius* p *having the point* P *for its centre, and then taking the limit of the result when* p *is made to tend to infinity.*

The limit of course may or may not exist, but it will be seen from the examples given below that it does exist in an important class of cases, among which, so far as one can see, the case of the actual physical universe may very possibly be included.

Possible Failure of Gauss's Theorem.—Examples.

§ 4. *Ex.* 1.—The simplest possible case is that in which the density is uniform. For a sphere of uniform density the intensity at the centre is *nil*. If the radius is p, the limit of the value of the intensity for p tending to infinity is therefore also *nil*. Hence the definition just given makes the intensity zero everywhere ; and a potential V exists, namely V = constant.

It may be noted, in verification of the statement in the Introduction, that this value of V gives $\nabla^2 V = 4\pi(\rho - \rho)$, not $= 4\pi\rho$.

We may also test Gauss's Theorem by this case. Take any closed surface S. The intensity at the surface is 0. The integral of the normal intensity is therefore also 0, which is certainly not equal to $4\pi \times$ mass within S. Hence, *assuming Def. A*, Gauss's Theorem is incorrect when the field is infinite.

§ 5. For an infinite field, the definition of the intensity at a given point must involve a limit in some way or other, but of course many alternatives to Def. A are possible. The alternative next in naturalness to Def. A would differ from it only in having the centre of the sphere p at an arbitrary fixed point instead of at the point where the intensity is to be found. Subject to convergence conditions, this alternative definition would lead to Gauss's Theorem and the ordinary theory. Take for example once more the simple case of constant density. Choose the radius p so large that the surface S is entirely within the varying sphere. Denote the normal force at a point of S due to the matter within p by N_p. As in the usual proof, a particle of mass m within S contributes $4\pi m$ to the surface integral of N_p, but a particle outside S, though still within p, contributes nothing. Hence

$$\iint N_p \, dS = 4\pi \text{ (mass within S)}.$$

Since a uniform spherical shell exerts no force at a point in the hollow of the shell, N_p does not change as p increases,

so that it tends to its limit uniformly over S, and we therefore have

$$\iint \mathrm{N}\, d\mathrm{S} = 4\pi \text{ (mass within S)},$$

which is Gauss's theorem ; and from this Poisson's equation follows at once.

Note that, with Def. A, the sphere p varies from point to point of S, so that this method could not be applied.

At a superficial glance it may seem that the usual proof of Gauss's Theorem should hold good whether the field is finite or not, irrespective of any supplement to the law to meet the case of the field being infinite. For the proof is: an internal mass m contributes $4\pi m$, but an external mass nothing, to the surface integral, and the integral must therefore be equal to 4π (total internal mass).

The fallacy lies, of course, in the assumption that a process (such as change in the order of integration or summation) which is legitimate for finite integrals and sums can also be applied without question to infinite integrals and series. Thus, if $\mathrm{F(P, Q)}\, dm$ denotes the inward normal force at a point P of the surface S, due to the element of mass dm at any point Q outside S, the above "proof" takes for granted that

$$\iint [\int \mathrm{F(P, Q)}\, dm]\, d\mathrm{S} = \int [\iint \mathrm{F(P, Q)}\, d\mathrm{S}]\, dm ;$$

the argument being that—since for a fixed dm (outside S) we have

$$\iint \mathrm{F(P, Q)}\, d\mathrm{S} = 0,$$

so that the integrand on the right, and therefore the integral on the right, vanishes—therefore the integral on the left (exists and) vanishes. But the simple example given at the end of § 4 shows that the inference may be quite erroneous.

It may be worth observing also that if the above argument were sound, we should be proving a definite property of the gravitational intensity before we had even defined it.

§ 6. The example considered in §§ 4, 5—density constant throughout infinite space—is certainly trivial, but it is sufficient to bring out clearly the essential points of difference between the ordinary theory and the one now being proposed. According to the latter, when ρ is constant, a particle, no matter where situated, is not attracted at all. According to the theory which starts from Poisson's equation, the simplest value of the potential is

$$\mathrm{V} = \frac{2\pi}{3}\rho(x^2 + y^2 + z^2),$$

and the force on a given particle depends on the choice of an arbitrary origin at which the force shall vanish ; and there is obviously no upper bound to the differences of potential which occur.

If we take the view that no point of space is to be privileged above another, there seems to be no question which theory is to be preferred.

§ 7. *Ex.* 2.—Let ρ be everywhere constant as before, except for a spherical cavity with centre O and radius a. For any point P we can always take the radius p large enough to include the cavity. If this were filled up, the intensity at P would be zero ; the actual force, if P is outside the cavity, is therefore a repulsion from O of amount $\frac{4}{3}\pi\rho a^3 \cdot \mathrm{OP}/\mathrm{OP}^3$: and the potential at any point is that due to a sphere of radius a, centre O, and density $(-\rho)$. In this example also, the equation for the potential is

$$\nabla^2 \mathrm{V} = 4\pi(\rho - \bar{\rho}).$$

§ 8. *Ex.* 3.—Let $\rho = \cos(lx + my + nz + \alpha)$, where x, y, z are rectangular coordinates and l, m, n, α are constants. For the calculations we may work with $\rho = e^{i(lx+my+nz)}$, or, by simply changing the axes, with $\rho = e^{ikz}$, where $k = \sqrt{(l^2+m^2+n^2)}$.

To calculate the component intensities I_x, I_y, I_z at $\mathrm{P}(x, y, z)$ when $\rho = e^{ikz}$, we surround P with a sphere of radius p, at any point $(x+\mathrm{X}, y+\mathrm{Y}, z+\mathrm{Z})$ of which the density is $\rho(x+\mathrm{X}, y+\mathrm{Y}, z+\mathrm{Z})$ or $e^{ikz} \cdot e^{ik\mathrm{Z}}$. We then have, denoting by $\mathrm{I}_z(p)$ the z-intensity from the sphere p,

$$\mathrm{I}_z(p) = e^{ikz} \iiint_p e^{ik\mathrm{Z}} (\mathrm{Z}/\mathrm{R}^3)\, d\mathrm{X}\, d\mathrm{Y}\, d\mathrm{Z},$$

where $\qquad \mathrm{R} \equiv \sqrt{(\mathrm{X}^2+\mathrm{Y}^2+\mathrm{Z}^2)},$

and the subscript p indicates that the volume integral is taken through the sphere $\mathrm{X}^2+\mathrm{Y}^2+\mathrm{Z}^2 = p^2$.

Changing to polar coordinates R, θ, ϕ we find

$$\mathrm{I}_z(p) = e^{ikz} \iiint_p e^{ik\mathrm{R}\cos\theta} \cos\theta \sin\theta\, d\mathrm{R}\, d\theta\, d\phi$$

$$= e^{ikz} \cdot 2\pi \int_0^\pi \sin\theta\, d\theta \int_0^p e^{ik\mathrm{R}\cos\theta} \cos\theta\, d\mathrm{R}$$

$$= e^{ikz} \cdot 2\pi \int_0^\pi \sin\theta\, d\theta\, (e^{ikp\cos\theta} - 1)/ik$$

$$= e^{ikz} \cdot 2\pi \left\{ \frac{e^{ikp} - e^{-ikp}}{ikp} - 2 \right\} \Big/ ik$$

$$= (4\pi/ik) \left\{ (\sin kp)/(kp) - 1 \right\} e^{ikz}.$$

By Def. A (§ 3) the intensity I_x at P is the limit of $I_z(p)$ when $p \to \infty$. Hence

$$I_z = (4\pi i/k) e^{ikz}.$$

On writing down the expressions for $I_x(p)$ and $I_y(p)$ it will be seen at once that they vanish ; thus

$$I_x = I_y = 0.$$

The field is therefore derivable from the potential $(-4\pi/k^2)e^{ikz}$.

The quantity of matter in the sphere p is

$$e^{ikz} \iiint_p e^{ikZ}\, dX\, dY\, dZ$$

$$= e^{ikz}(4\pi/k^3)(\sin kp - kp \cos kp)$$

which is of order p.

The corresponding results for $\rho = \cos(lx + my + nz + \alpha)$ are obtained from these at once by taking the real parts, and changing k into $\sqrt{(l^2 + m^2 + n^2)}$, and kz into $lx + my + nz + \alpha$.

The example does not immediately apply to gravitation, since negative densities occur. But this defect is remedied in a moment by adding a constant A to the given ρ, where A is any positive number not less than 1. By § 4, this makes no change in the intensity or in the potential at any point.

The total quantity of matter in the sphere p will now be

$$\tfrac{4}{3}\pi p^3 A + \text{the term of order } p \text{ already found},$$

so that the mean density $\bar{\rho}$ is A.

Thus, for

$$\rho = A + e^{ikz},$$

the potential V is

$$(-4\pi/k^2)e^{ikz} ;$$

so that

$$\nabla^2 V = 4\pi e^{ikz}$$

$$= 4\pi(\rho - \bar{\rho}),$$

as in the simpler examples already given.

It is obvious that a density represented by the sum of a finite number of terms of the above type,

$$A+\cos(lx+my+nz+\alpha),$$

each multiplied by a positive constant, will again give a finite potential V satisfying the equation

$$\nabla^2 V=4\pi(\rho-\bar{\rho}).$$

Clearly a distribution of considerable generality could be built up in this way, and it might be interesting to attempt to carry the investigation further on these lines, from the point of view of a Fourier integral representing the density. But the analysis would be very delicate, and we can obtain all we want in a much more elementary way, as in the succeeding paragraphs.

Problem—Potential given, Density required.

§ 9. Before taking up the final problem of determining the potential (when it exists) of a given distribution of matter, we shall first consider the simpler case when it is the potential that is given, and it is required to determine the distribution of matter which—always on the basis of the definition of § 3—will produce this potential.

Suppose that we are given a function u of x, y, z which is finite and continuous throughout all space (so that there is an assignable positive number μ which the numerical value of u never exceeds), and which has first and second derivatives possessing these same properties.

We shall calculate the potential due to a distribution of matter with density

$$\rho'=\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}.$$

In general it will turn out that this value of ρ' takes negative values as well as positive, but we shall get over the difficulty by the same artifice as in § 8. Following the method already used there, we calculate the component intensity $I_z(p)$ at (x, y, z) due to the density $\rho'(x+X, y+Y, z+Z)$ throughout the sphere $X^2+Y^2+Z^2=p^2$.

Write u simply for

$$u(x+X,\ y+Y,\ z+Z),$$

and $\nabla^2 u$ for

$$\frac{\partial^2 u}{\partial X^2}+\frac{\partial^2 u}{\partial Y^2}+\frac{\partial^2 u}{\partial Z^2}.$$

Then $$I_z(p) = \iiint_p \nabla^2 u (Z/R^3)\, dX\, dY\, dZ.$$

We now apply Green's Theorem, in the form

$$\iiint (\alpha \nabla^2 \beta - \beta \nabla^2 \alpha)\, dX\, dY\, dZ = \iint \left(\alpha \frac{\partial \beta}{\partial \nu} - \beta \frac{\partial \alpha}{\partial \nu}\right) dS,$$

taking $\alpha = Z/R^3$, $\beta = u$, to the field obtained from the sphere p by cutting out an infinitesimal concentric sphere of radius ϵ.

From the conditions imposed on u, we have, over the surface of the sphere ϵ,

$$\beta = u(x, y, z) + \left(X\frac{\partial}{\partial x} + Y\frac{\partial}{\partial y} + Z\frac{\partial}{\partial z}\right) u(x, y, z)$$
$$+ \text{a remainder of order } \epsilon^2; \text{ and}$$

$$\frac{\partial \beta}{\partial \nu} = -\frac{1}{\epsilon}\left(X\frac{\partial}{\partial x} + Y\frac{\partial}{\partial y} + Z\frac{\partial}{\partial z}\right) u(x, y, z)$$
$$+ \text{a remainder of order } \epsilon.$$

Hence, when $\epsilon \to 0$, the limit of

$$\iint \left(\alpha \frac{\partial \beta}{\partial \nu} - \beta \frac{\partial \alpha}{\partial \nu}\right) dS_\epsilon$$
$$= \mathrm{Lt} \iint \left\{ (Z\epsilon^3)(-Z\epsilon) - Z(2Z\epsilon^4) \right\} \frac{\partial}{\partial z} u(x, y, z)\, dS_\epsilon$$
$$= -4\pi \frac{\partial}{\partial z} u(x, y, z).$$

Thus, noting that $\nabla^2 \alpha = 0$, we find

$$I_z(p) = -4\pi \frac{\partial}{\partial z} u(x, y, z) + \iint \left(\frac{Z}{R^3}\frac{\partial u}{\partial R} + \frac{2Z}{R^4} u\right) dS_p.$$

Since u is finite, the part of the surface integral arising from the second term is of order $1/p$ and vanishes in the limit when $p \to \infty$.

The remaining part

$$= \frac{1}{p^3} \iint Z \frac{\partial u}{\partial R}\, dS_p$$
$$= \frac{1}{p^3} \iint u \frac{\partial Z}{\partial R}\, dS_p + \frac{1}{p^3} \iiint_p Z \nabla^2 u\, dX\, dY\, dZ,$$

by Green's Theorem.

The first term on the right is again of order $1/p$, so that, making $p \to \infty$, we have

$$I_z = -4\pi \frac{\partial}{\partial z} u(x, y, z),$$

provided

$$\operatorname*{Lt}_{p\to\infty} \frac{1}{p^3} \int_{-p}^{p}\int_{-p}^{p}\int_{-p}^{p} Z\nabla^2 u \, dX \, dY \, dZ = 0. \quad . \quad . \quad . \quad (1)$$

Since

$$\int_{-p}^{p}\int_{-p}^{p}\int_{-p}^{p} \nabla^2 u \, dX \, dY \, dZ = \int\int \frac{\partial u}{\partial R} \, dS_p,$$

which is of order p^2, the average density of the matter in the sphere p tends to 0 when $p \to \infty$. But, as already indicated, we may add to the density a constant positive term A, large enough to ensure that the sum is nowhere negative; the density ρ is now $A + \rho'$, so that $\rho' = \rho - A$, or (since A is now evidently the mean density) $\rho' = \rho - \bar{\rho}$.

Thus, provided u satisfies the condition (1), as well as the conditions stated near the beginning of this § 9, the gravitational field calculated directly from Newton's Law in accordance with Def. A for a density

$$\rho = \bar{\rho} + \frac{1}{4\pi}\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right)$$

has for its potential the function $u(x, y, z)$. The constant $\bar{\rho}$ is the limiting mean density of matter in any indefinitely increasing sphere with fixed centre, and the equation satisfied by the potential is

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = 4\pi(\rho - \bar{\rho}).$$

Sufficient Conditions for Finite Potential.

§ 10. We now come to our main problem, viz., to determine sufficient conditions that a given distribution of matter should produce a potential which is everywhere finite, and to obtain an analytical expression for the potential when these conditions are satisfied—again on the understanding that the intensity is calculated from Newton's Law as in Def. A.

Let the density at (x, y, z) be $\rho(x, y, z)$. It will be assumed that ρ and its first derivatives are continuous throughout, the analysis being thus considerably shortened.

With the notation already used in §§ 8, 9 we have

$$I_z(p) = \iiint_p \rho(x+X, y+Y, z+Z)\,(Z/R^3)\,dX\,dY\,dZ.$$

Ignoring explicit reference to x, y, z for the moment, put

$$\iiint_p \rho(x+X, y+Y, z+Z)\,Z\,dX\,dY\,dZ = f(p);$$

then

$$\iint \rho(x+X, y+Y, z+Z)\,Z\,dS_p = \frac{\partial}{\partial p} f(p) = f'(p),$$

and

$$I_z(p) = \int_0^p f'(R)\,dR/R^3.$$

Hence

$$I_z(q) - I_z(p) = \int_p^q f'(R)\,dR/R^3$$
$$= f(q)/q^3 - f(p)/p^3 + 3\int_p^q f(R)\,dR/R^4.$$

Suppose now that $f(R)/R^3 \to 0$ when $R \to \infty$; or rather, with closer restriction, that for all values of R > some fixed value R_0 we have

$$|f(R)| < MR^{3-s}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where M and s are fixed positive numbers.

It obviously follows that $I_z(q) - I_z(p)$ can be made as small numerically as we please, by taking p large enough and $q > p$. In other words $\lim_{p\to\infty} I_z(p)$ exists, *i. e.*, the density ρ gives rise to intensities which are everywhere finite.

§ 11. Suppose next that the mean density within the sphere p, viz.

$$\iiint_p \rho(x+X, y+Y, z+Z)\,dX\,dY\,dZ / \tfrac{4}{3}\pi p^3,$$

tends, when $p \to \infty$, to a limit $\bar{\rho}$, independent of x, y, z; and consider the integral

$$E_p = -\iiint_p \{\rho(x+X, y+Y, z+Z) - \bar{\rho}\}(1/R)\,dX\,dY\,dZ.$$

If we write

$$\iiint_p \{\rho(x+X, y+Y, z+Z) - \bar{\rho}\}\,dX\,dY\,dZ = \psi(p),$$

then

$$E_p = -\int_0^p \psi'(R)\, dR/R\,;$$

and

$$\int_p^q \psi'(R)\, dR/R = \psi(q)/q - \psi(p)/p + \int_p^q \psi(R)\, dR/R^2.$$

Suppose that, when $R > R_0$,

$$|\psi(R)| < M_1 R^{1-s_1}, \quad \ldots\ldots \quad (3)$$

where M_1, s_1 are fixed positive numbers.

Then, as in the similar case of § 10, $\operatorname{Lt}_{p\to\infty} E_p$ exists; we shall denote it by $E(x, y, z)$.

§ 12. Write

$$\rho_1(x, y, z) \quad \text{for} \quad \rho(x, y, z) - \bar{\rho}.$$

Returning to § 10, we have, by one form of Green's Theorem, noting that

$$\iiint_p \bar{\rho}(dR^{-1}/dZ)\, dX\, dY\, dZ = 0,$$

$$\begin{aligned} I_z(p) &= -\iiint_p \rho(x+X, y+Y, z+Z)(dR^{-1}/dZ)\, dX\, dY\, dZ \\ &= -\iiint_p \rho_1(x+X, y+Y, z+Z)(dR^{-1}/dZ)\, dX\, dY\, dZ \\ &= \iiint_p R^{-1}(\partial\rho_1/\partial Z)\, dX\, dY\, dZ - \iint n R^{-1}\rho_1\, dS_p, \end{aligned}$$

where n is the z-direction cosine of the normal to S_p. We can replace the surface integral by the volume integral

$$\frac{1}{p}\iiint_p \frac{\partial}{\partial Z}\rho_1(x+X, y+Y, z+Z)\, dX\, dY\, dZ\,;$$

and clearly $\qquad \partial\rho_1/\partial Z = \partial\rho_1/\partial z.$

We therefore have

$$I_z(p) = \frac{\partial}{\partial z}\left\{\iiint_p (\rho_1/R)\, dX\, dY\, dZ - \frac{1}{p}\iiint \rho_1\, dX\, dY\, dZ\right\}.$$

Integrate this equation from z_0 to z, keeping x, y constant. Thus

$$\int_{z_0}^{z} \mathrm{I}_z(p)\,dz = \left| \begin{array}{l} \iiint_p (\rho_1/\mathrm{R})\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z} \\ -(1/p)\iiint_p \rho_1\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z} \end{array} \right| \begin{array}{l} x, y, z \\ x, y, z_0. \end{array}$$

Now let $p \to \infty$. If the numbers M and s of § 10 are fixed throughout the field, $\mathrm{I}_z(p)$ tends *uniformly* everywhere to its limit I_z, so that

$$\int_{z_0}^{z} \mathrm{I}_z(p)\,dz \to \int_{z_0}^{z} \mathrm{I}_z\,dz.$$

As for the other side of the equation, we have already postulated, at § 11 (3), that

$$(1/p)\iiint_p \rho_1\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z} \to 0.$$

Hence

$$\int_{z_0}^{z} \mathrm{I}_z\,dz = \operatorname*{Lt}_{p\to\infty} \left| \iiint_p (\rho_1/\mathrm{R})\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z} \right| \begin{array}{l} x, y, z \\ x, y, z_0 \end{array}$$

$$= -\mathrm{E}(x, y, z) + \mathrm{E}(x, y, z_0),$$

from § 11. Thus

$$\mathrm{I}_z = -\frac{\partial \mathrm{E}}{\partial z};$$

and similarly,

$$\mathrm{I}_x = -\frac{\partial \mathrm{E}}{\partial x}, \qquad \mathrm{I}_y = -\frac{\partial \mathrm{E}}{\partial y},$$

so that the field has the potential E.

Deduction of the Modified Poisson's Equation.

§ 13. We now come to the final step of the analysis, the investigation of the differential equation for the potential.

For finite systems, we have Poisson's equation

$$\nabla^2 \mathrm{E} = 4\pi\rho.$$

For the infinite systems under consideration, and of course as a special case for finite systems also, it will now be shown that the corresponding equation is

$$\nabla^2 \mathrm{E} = 4\pi(\rho - \bar{\rho}),$$

where $\bar{\rho}$ is (§ 11) the mean density over the whole of space (so that $\bar{\rho}=0$ for finite systems).

This equation is the same as

$$\frac{\partial \mathrm{I}_x}{\partial x}+\frac{\partial \mathrm{I}_y}{\partial y}+\frac{\partial \mathrm{I}_z}{\partial z}=-4\pi(\rho-\bar{\rho})$$
$$=-4\pi\rho_1, \text{ say,}$$

where (§ 10)

$$\mathrm{I}_z=\operatorname*{Lt}_{p\to\infty}\mathrm{I}_z(p),$$

with

$$\mathrm{I}_z(p)=-\iiint_p \rho(x+\mathrm{X}, y+\mathrm{Y}, z+\mathrm{Z})(d\mathrm{R}^{-1}/d\mathrm{Z})\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z};$$

here we may, as at the beginning of § 12, write ρ_1 instead of ρ without changing the value of the integral.

For convenience in calculating the derivative $\partial \mathrm{I}_z/\partial z$, this integral will now be modified by cutting out from the field of integration a small sphere of radius ϵ round (x, y, z) as centre. Thus

$$\mathrm{I}_z=\operatorname*{Lt}_{p\to\infty,\ \epsilon\to 0}\mathrm{I}_z(p, \epsilon),$$

where $\mathrm{I}_z(p, \epsilon)$ only differs from $\mathrm{I}_z(p)$ by the excision of the volume of the sphere ϵ, and p, ϵ go to their limits independently; and we write

$$\mathrm{I}_z(p, \epsilon)=-\iiint_{p,\epsilon}\rho_1(x+\mathrm{X}, y+\mathrm{Y}, z+\mathrm{Z})(d\mathrm{R}^{-1}/d\mathrm{Z})\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z}.$$

This gives

$$\frac{\partial}{\partial z}\mathrm{I}_z(p, \epsilon)=-\iiint_{p,\epsilon}\frac{\partial \rho_1}{\partial \mathrm{Z}}\frac{\partial \mathrm{R}^{-1}}{\partial \mathrm{Z}}\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z},$$

since $$\partial\rho_1/\partial z=\partial\rho_1/\partial \mathrm{Z}.$$

We may not infer at once that

$$\operatorname*{Lt}_{p\to\infty,\ \epsilon\to 0}\frac{\partial}{\partial z}\mathrm{I}_z(p, \epsilon)$$

exists, and is equal to $\partial \mathrm{I}_z/\partial z$. Some such analysis as the following is first necessary.

By Green's Theorem we have

$$\frac{\partial}{\partial z}\mathrm{I}_z(p, \epsilon)=\iiint_{p,\epsilon}\rho_1\frac{\partial^2 \mathrm{R}^{-1}}{\partial \mathrm{Z}^2}\,d\mathrm{X}\,d\mathrm{Y}\,d\mathrm{Z}$$
$$=\Big|\iint\frac{\mathrm{Z}}{\mathrm{R}}\rho_1\frac{\partial \mathrm{R}^{-1}}{\partial \mathrm{Z}}\,d\mathrm{S}\Big|_{\epsilon}^{p}.$$

Put

$$J_z(p,\epsilon)=\iiint_{p,\epsilon}\rho_1(x+X,y+Y,z+Z)(d^2R^{-1}/dZ^2)\,dX\,dY\,dZ.$$

We first specify sufficient conditions that $J_z(p,\epsilon)$ may tend to a limit J_z, and that uniformly as regards z, when p and ϵ tend to their limits.

We have

$$J_z(p,\epsilon)=\iiint_{p,\epsilon}\rho_1(x+X,y+Y,z+Z)(3Z^2-R^2)R^{-5}\,dX\,dY\,dZ.$$

Write

$$\iiint_{p}\rho_1(x+X,y+Y,z+Z)(3Z^2-R^2)\,dX\,dY\,dZ=\chi(p).$$

Then

$$\iint\rho_1.(3Z^2-R^2)\,dS_p=\chi'(p),$$

and

$$J_z(q,\epsilon)-J_z(p,\epsilon)=\int_p^q\chi'(R)\,dR/R^5$$
$$=\chi(q)/q^5-\chi(p)/p^5+5\int_p^q\chi(R)\,dR/R^6.$$

Assume

$$|\chi(R)|<M_2R^{5-s_2},\quad\ldots\ldots\quad(4)$$

when $R>R_0$, where M_2 and s_2 are positive numbers independent of x,y,z; not an onerous condition, seeing that $\chi(R)$ is of order not higher than R^5, even if ρ_1 is subjected only to the condition of finiteness.

Then $J_z(q,\epsilon)-J_z(p,\epsilon)$ clearly $\to 0$ as p and $q\to\infty$, and that uniformly with respect to z; the uniform convergence at the ϵ end is easily proved on replacing $\rho_1(x+X,y+Y,z+Z)$ by the sum of $\rho_1(x,y,z)$ and a remainder term of the first order as in Taylor's Theorem, and changing to polar coordinates.

Hence $J_z(p,\epsilon)$ tends, uniformly as to z, to a limit, say $J_z(x,y,z)$ or J_z.

Return now to the equation

$$\frac{\partial}{\partial z}I_z(p,\epsilon)=J_z(p,\epsilon)$$
$$-\left|\iint\int_R^Z\rho_1(x+X,y+Y,z+Z)\frac{\partial R^{-1}}{\partial Z}dS\right|_\epsilon^p.$$

The contribution to the last term of this equation from the ϵ surface is

$$-\iint \frac{Z}{R}\rho_1 \frac{Z}{R^3} dS_\epsilon.$$

Call this t_ϵ; its limit, when $\epsilon \to 0$, is $-\frac{4\pi}{3}\rho_1(x, y, z)$.

From the p surface the last term of the equation gives

$$\frac{1}{p^3}\iint \frac{Z}{R}\rho_1(x+X, y+Y, z+Z)Z\, dS_p,$$

which, by Green's Theorem, is equal to

$$\frac{1}{p^3}\iiint_p \frac{\partial}{\partial Z}(Z\rho_1)\, dX\, dY\, dZ$$

$$= \frac{1}{p^3}\iiint_p \rho_1\, dX\, dY\, dZ + \frac{1}{p^3}\frac{\partial}{\partial z}\iiint_p Z\rho_1\, dX\, dY\, dZ.$$

It will be shown that the two terms on the right will disappear from the final result. Write them briefly as $T_1 + (\partial/\partial z)T_2$; it has already been postulated that T_1 (§ 11) and T_2 (§ 10) $\to 0$ when $p \to \infty$.

Resuming all the terms of the equation for $(\partial/\partial z)I_z(p, \epsilon)$, we have now

$$\frac{\partial}{\partial z}I_z(p, \epsilon) = J_z(p, \epsilon) + t_\epsilon + T_1 + \frac{\partial}{\partial z}T_2.$$

Hence, integrating from z_0 to z, we get

$$\Big| I_z(p, \epsilon) - T_2 \Big|_{z_0}^{z} = \int_{z_0}^{z} \Big\{ J_z(p, \epsilon) + t_\epsilon + T_1 \Big\}\, dz.$$

Now let p and ϵ tend to their limits. We have seen that $J_z(p, \epsilon) \to J_z$, $t_\epsilon \to -\frac{4\pi}{3}\rho_1(x, y, z)$, $T_1 \to 0$, $T_2 \to 0$, $I_z(p, \epsilon) \to I_z$; and all, the first three in particular, uniformly as to z. Thus

$$I_z - I_{z_0} = \int_{z_0}^{z} \Big\{ J_z - \frac{4}{3}\pi\rho_1(x, y, z) \Big\}\, dz,$$

and, by differentiation,

$$\frac{\partial I_z}{\partial z} = J_z - \frac{4}{3}\pi\rho_1(x, y, z).$$

A single step more gives us the result we seek. For we have, from the definition of $J_z(p, \epsilon)$,

$$\begin{aligned} &J_x(p, \epsilon) + J_y(p, \epsilon) + J_z(p, \epsilon) \\ &= \iiint_{p, \epsilon} \rho_1(x+X, y+Y, z+Z) \\ &\qquad \left(\frac{\partial^2 R^{-1}}{\partial X^2} + \frac{\partial^2 R^{-1}}{\partial Y^2} + \frac{\partial^2 R^{-1}}{\partial Z^2}\right) dX\, dY\, dZ \\ &= 0. \end{aligned}$$

Hence, taking the limits, we have

$$J_x + J_y + J_z = 0,$$

and therefore

$$\frac{\partial I_x}{\partial x} + \frac{\partial I_y}{\partial y} + \frac{\partial I_z}{\partial z} = -4\pi\rho_1(x, y, z),$$

or finally (§ 12)

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = 4\pi(\rho - \bar{\rho}),$$

the result required.

Interpretation of Conditions for Finite Potential.

§ 14. The conditions (3), (2), (4) have an obvious and interesting dynamical interpretation. To speak in the broadest possible terms, they may be regarded as stating that—

(i.) The average density of matter is the same round every point of space;

(ii.) Every point is a centre of inertia;

(iii.) Every axis is a principal axis of inertia.

It is a curious fact, on which a little reflexion might not be wasted, that these are just the sort of conditions which, on the basis of Newtonian dynamics, we should expect to be fulfilled if the present distribution and motion of matter have arisen, in consequence of some initial disturbance, from a primæval uniform distribution at rest in infinite Euclidean space.

Further, on the assumption that gravitation is propagated with a finite velocity, say c, it is clear that matter at a greater spatial distance than $c\mathrm{T}$ would have no effect, T being the

distance in time of the original disturbance. In these circumstances, the Newtonian gravitational intensity could hardly be defined in any other way than in Def. A, modified of course for "retardation."

Application to Relativity.

§ 15. The chief point of interest about the suggested modification of Poisson's equation is doubtless its bearing upon the General Theory of Relativity, an essential step in the usual presentation of which is the proof that Einstein's equations reduce in a first approximation to the ordinary equations of Newtonian dynamics, including in particular Poisson's equation $\nabla^2 V = 4\pi\rho$. If the latter equation is to be replaced by $\nabla^2 V = 4\pi(\rho - \bar{\rho})$, it would seem reasonable to make a corresponding change in the equations of relativity, *i. e.* in the set of equations *

$$G_{\mu\nu} - \tfrac{1}{2} g_{\mu\nu} G = -8\pi T_{\mu\nu}.$$

The natural change to make is to replace $T_{\mu\nu}$ by $T_{\mu\nu} - \overline{T}_{\mu\nu}$, where $\overline{T}_{\mu\nu}$ is some tensor of the second order, connected with the matter in the field. The tensor $\overline{T}_{\mu\nu}$ should be in some sense a mean, or smoothed-out, form of $T_{\mu\nu}$, but, of course, we cannot define it literally as the mean of $T_{\mu\nu}$, since the mean value of a tensor is not itself a tensor. A constant multiple of $g_{\mu\nu}$ might serve.

For our purpose one condition is essential. If, with Eddington, we assume the proper density ρ to be given by

$$\rho = T,$$

T being the invariant $g^{\mu\nu} T_{\mu\nu}$, then we must impose on $T_{\mu\nu}$ the condition

$$\overline{T} = \bar{\rho},$$

where $\overline{T} = g^{\mu\nu} \overline{T}_{\mu\nu}$, and ρ is the mean density, which we assume to exist, and which will be given as the limit of the ratio of the integrals

$$\int \sqrt{-g}\rho \, dx_1 \, dx_2 \, dx_3 \, dx_4$$

and

$$\int \sqrt{-g} \, dx_1 \, dx_2 \, dx_3 \, dx_4,$$

* The notation and units are essentially those of Eddington's 'Mathematical Theory of Relativity.'

taken over a region of space-time increasing indefinitely in every direction from any assigned origin.

We shall then have the usual first approximation to the metric of space-time in the form

$$ds^2=(1+2V)\,dx_4^2-(1-2V)(dx_1^2+dx_2^2+dx_3^2);$$

but the equation for V will now be

$$\nabla^2 V=4\pi(\rho-\bar{\rho}).$$

The point to be emphasized is that this equation may have a solution which is finite *everywhere*, so that the above approximation to ds^2 is no longer of merely local application, but may hold good throughout the whole of space-time.

From this point of view, the curvatures represented by the gravitational tensor are not related directly to the energy tensor itself, but to its deviation from uniformity. The mean curvature has one sign where there is matter, and the opposite sign where there is none. On the large scale, the deviations from flatness balance each other, so that *space-time on the whole is approximately Galilean throughout*, and in particular space is roughly Euclidean to infinity.

Since $\bar{\rho}$ is excessively minute—Hubble estimates the mean density of matter at $1{\cdot}5\times10^{-31}$ gr. per c.c.—the ordinary applications within the solar system are not interfered with.

Summary.

Newton's Law of the inverse square must be supplemented before it can be applied to a distribution of matter extending to infinity. The procedure which seems most natural leads to a modification of Poisson's equation which, though unimportant for ordinary applications, is of considerable significance cosmologically, since it allows the possibility of a gravitational potential and intensity everywhere finite, even when the distribution of matter is of broadly uniform character throughout all space. A similar modification is suggested for the equations of General Relativity. The main effect of this would be that the world would be macroscopically Galilean, so that space would be Euclidean instead of having a small constant positive curvature as in Einstein's theory.

IX. *Magnetism and Molecular Structure.*—Part I. *The Magnetic Susceptibilities of some Liquid Organic Isomers.* *By* Prof. S. S. Bhatnagar, *D.Sc.*(*Lond.*), *F.Inst. Phys.*, Ram Narain Mathur, *M.Sc.*, *and* Ram Sahai Mal, *M.Sc.**

THE relation between magnetic susceptibilities and chemical constitution of organic compounds has been considerably investigated. Henrichsen [1] showed that the "magnetization numbers" of organic compounds can be calculated additively from the values for the component atoms. Besides other substances, he tried some isomeric compounds and found that the values of the magnetic susceptibilities for the normal and iso compounds were always the same. And the values for ortho, meta, and para compounds should also be the same according to his views. Again, according to Meyer [2], the isomeric substances have, at least to a first approximation, no difference in their "magnetization numbers." Meslin [3] also determined the specific magnetic susceptibility of a large number of organic compounds, and compared his results with those of Plücker, Faraday, Becquerel, Quincke, and Henrichsen. The only isomeric substances in his tables of data are butyl and iso-butyl alcohols, and the latter is a little more diamagnetic then the former. The influence of chemical constitution on magnetic properties was also extensively studied by Pascal [4]. His general results confirm Henrichsen's [5] observations that the magnetic properties of organic liquids are additive in character, *i. e.*, the molecular susceptibility $x_m = \Sigma a x_\lambda + \lambda$ where a is the number of atoms of susceptibility, x_λ and λ is a constitutive constant depending on the nature of the linkages between the atoms. The values of x_m should therefore be the same for isomeric substances.

But when we examine the physical properties of organic isomers, we find that their densities, boiling-points, surface-tensions, refractive indices, and viscosities are never exactly the same. According to Perkin [6], even their molecular magnetic rotations are different. The experiments of Krishnan [7], Rama Krishna Rao [8], and others on the scattering of light show that their depolarization

* Communicated by the Author.

factors are not the same. Stewart [9] examined them by the X-ray diffraction ionization method and found different results for them. Sogani [10] and Krishnamurti [11] also observed differences between the X-ray diffraction liquid haloes of isomeric molecules. Even the ultra-violet absorption spectra [12] and the Raman spectra [13] of the isomeric xylenes and the primary and secondary alcohols show that isomerides are distinguishable from each other. In view of these facts it became interesting to examine the isomers regarding their magnetic properties on a sensitive magnetic balance and to see whether these properties can be co-related with their other physical properties and with the views expressed in previous papers from this laboratory [14] on the subject of electronic isomers.

Experimental.

The apparatus employed during this investigation is similar to Bauer and Piccard's [15] U-tube apparatus (Method I.) with this difference, that the sides of both the reservoir and the tube, except near the two ends, are made double-walled. Readings for any temperature of the liquid under investigation are taken by circulating water from a thermostat, electrically maintained at the desired temperature, in the outer jackets around the tube and the reservoir. Before taking readings water is allowed to flow till the liquid under investigation attains the desired constant temperature. The portion of the narrow tube in between the pole-pieces is not double-walled. And, in order to prevent any variation in temperature at the meniscus, it is necessary that the atmosphere around it should be at about the same temperature. The portion of the narrow tube from a little above the meniscus was therefore surrounded by a small glass condenser through which water, at the same temperature as that passing through the rest of the apparatus, was circulated.

Again, as in Bauer and Piccard's apparatus, the reservoir could be moved up and down by means of a fine screw. But on applying magnetic field, the actual rise or fall of the meniscus was observed by a microscope. As the differences between the deflexions of the meniscus for the isomeric liquids are very small, a micrometer eyepiece was used. In doing the actual experiments, it was also observed that very small changes in the position of the

narrow tube and the meniscus in the field affect the results. It was, therefore, necessary to put the tube every time after cleaning in exactly the same position. A brass plate was therefore fixed to the top of the pole-pieces of the electromagnet, and a hole was bored in it so that the narrow tube could just pass through it. This served to check any big change in the position of the tube in the field. To avoid small displacements, a fine cross-mark was etched on the narrow tube, and its position was noticed by a fixed microscope and kept the same. For every reading the meniscus was brought to the same position in the field by raising or lowering the reservoir by means of a fine screw, and every precaution was taken to ensure that the readings for isomerides and water are always taken in the same position of the tube and the meniscus in the field. Scrupulous care was also taken in cleaning the tube and the bottle to prevent any sticking of the liquid, and a constant current was passed in the electromagnet. The values of the magnetic susceptibility x were calculated by the equation

$$x = \frac{2\theta g}{H^2} + x\frac{\rho_0}{\rho},$$

where

x = specific susceptibility of the liquid,

x_0 = specific susceptibility of air (210×10^{-7}),

ρ_0 = density of air,

ρ = density of the liquid, and

θ = displacement of the meniscus.

The apparatus was standardised with respect to water ($x = -7{\cdot}25 \times 10^{-7}$).

Estimation of the Purity of Substance investigated.

The differences between the susceptibilities of isomerides are of very small order, and it is therefore absolutely necessary that the substances investigated be quite pure. As water is a very common impurity in some of the substances used, its absence was made sure of by four or five tests. Absence of iron was also carefully tested for. Very elaborate precautions were taken in purifying the

substances. The difficulty chiefly arose from the isomerides being associated with each other, and great care had to be taken in separating them. As the methods of purification and estimation are different in each case, they are given below briefly and separately for the substances investigated.

(a) *Alcohols.*—Kahlbaum's pure propyl and isopropyl and Merck's extra pure butyl alcohols were taken A very large amount of work on the purification of alcohols has been done by Brunel. Crenshaw and Tobin [16], Wildermann [17], Young and Fortey [18], Andrews [19], etc. And Kahlbaum and Merck's pure specimens further purified, according to the observations of workers named above, were used. In order to test for the impurities, the specimens were estimated volumetrically by the process of acetylation of the hydroxyl group by acetic anhydride. The results obtained, within the limits of experimental error, showed that the substances are quite pure. Absence of one isomeride in the other was also made sure of. Normal alcohol on oxidation gave aldehyde only, whereas the iso-alcohols gave acetone and no aldehyde. Any mixing of iso and tertiary isomerides was then tested for by means of their iodides (Meyer and Jacobsen's test).

(b) *Cresols* :—Merck's extra pure specimens were taken. In order to purify them they were distilled at their boiling-points. In the case of meta-cresol, it was cooled before distilling to 15° C. to remove all traces of ortho and para varieties, since they are solid at this temperature. Any mixing of ortho and para cresols was then tested for by means of their nitroso derivatives (Nolting and Kohn, vol. xvii. p. 351).

(c) *Nitro-toluenes.*—Same as for cresols.

(d) *Chloro-phenols.*—Kahlbaum's pure specimens further purified by distilling them at their boiling-points were used.

Physical constants like density, boiling-point, melting-point (where possible), and refractive index were also determined carefully for the substances investigated, and a comparison of our values with those given by other careful workers showed that the specimen used are quite pure.

Experimental Results.

The substances given in this investigation are all diamagnetic, but some of them have got double bonds in their structural formulæ to which the role of paramagnetism has been assigned by Pascal. It was also observed by us that the readings in some cases vary with temperature, and it was for this reason that the values for the different isomers have been taken at the same temperature. In the Table below are given the values at 34° C. except for ortho and para chlorophenol, for which the values are at

TABLE I.

Substance.	$x \times 10^7$
N-propyl alcohol	−7·94
Iso-propyl alcohol	−8·14
N-butyl alcohol	−8·25
Iso-butyl alcohol	−8·35
Tertiary butyl alcohol	−8·40
Ortho-cresol	−6·81
Meta-cresol	−6·69
Para-cresol*	−6·73
O-nitro toluene	−5·61
M-nitro toluene	−5·52
O-chlorophenol	−5·20
P-chlorophenol	−5·10

* Although its melting-point is 37° C., it can be kept liquid at 34° C. for a considerable time (*cf.* Perkin, J. C. S. vol. lxix. p. 1182, 1896).

45° C. The values have been calculated according to the formula given before, and are referred to water with $x = -7{\cdot}25 \times 10^{-7}$.

Discussion of Results.

It is clear from the preceding table that the values of x for isomerides are somewhat different. Sometimes the differences between these values are very small, for example, in the case of butyl and iso-butyl alcohols. But a series of experiments carried out in these special cases brought to our notice the interesting fact that the

differences were always in the same direction and real. Although Henrichsen (*loc. cit.*) and Meyer * found no change in the susceptibilities of isomerides, Meslin † has observed that the value of x for iso-butyl alcohol is greater than that for butyl alcohol. Pascal[20] has also observed at one place that there is a small increase in the diamagnetism in passing from a primary to a secondary and thence to a tertiary compound. His values for ethyl butyl iso-, butyl and tertiary butyl ketones come out to be $-7{\cdot}10\times10^{-7}$, $-7{\cdot}17\times10^{-7}$ and $-7{\cdot}20\times10^{-7}$, respectively. The values of x for the isomerides in the above stray observations, therefore, change in the same direction as observed by us. Again, if we examine the three values given above by Pascal for ethyl butyl ketones, we find that the values for secondary and tertiary isomerides are near together while a much larger difference exists between the value for primary and secondary isomerides. We have also examined the three isomerides of butyl alcohol, and we find that our values also for the secondary and tertiary isomerides are near together while a comparatively larger difference exists between the values for primary and secondary isomerides.

Again, according to the empirical equation[20] developed in previous papers from this laboratory, the value of the molecular magnetic susceptibility x_M is given by $x_M = -2{\cdot}85\times10^{10}\times k(r_1)^2$ where r_1 is the radius of the molecule and K is a constant depending on the number of electrons and atoms in the molecule. The values of this constant for isomeric substances will therefore be the same. Now according to the approximate methods of calculation used before, the values of the radii of two isomeric molecules will be the same. But it is apparent that on account of different constitutive forces the radii will always differ by a small amount. And, therefore, even according to the above equation, there should always be some difference between the values of x_M for isomeric substances as observed by us.

In order to get an idea of these constitutive forces attempts have been made by several workers to compare physical properties of compounds, especially organic, with their molecular constitution. Considerable discussion has centred round the relations between the boiling-points

* *Loc. cit.* † *Loc. cit.*

molecular volumes, and molecular constitution. Most of the properties of organic substances like molecular volume, molecular magnetic rotation, molecular refractivity, etc., have been shown to be additive in character with some constitutive factors. The magnetic susceptibilities of organic substances are also additive in character with certain constitutive factors. In the light of the above observations and those given in the introduction, it was

TABLE II.

Substance.	Boiling-point.	Depolarization factor, $r \times 100$.	Molecular volume.	Molecular magnetic susceptibility, $x_M \times 10^6$.	Molecular magnetic rotation.
N-propyl alcohol	97·3	7·1	81·3	—47·70	3·768
Iso-propyl alcohol	82·31	5·0	82·3	—48·91	4·019
N-butyl alcohol	117·42	9·3	101·8	—61·13	4·79 (calc.)
Iso-butyl alcohol	107·81	7·3	102·1	—61·87	4·936
Tertiary aclohol	82·22	4·1	102·4*	—62·24	5·122
O-cresol	190·8	..	121·5	—73·62	13·382
M-cresol	202·0	..	123·2	—72·32	12·776
P-cresol	201·0	..	123·5	—72·75	12·869
O-nitrotoluene	219·0	82	142·3	—76·94	10·806
M-nitrotoluene	230·6	83	144·0	—75·70	
O-chlorophenol	173·0	..	..	—66·83	
P-chlorophenol	217·0	..	..	—65·54	

* Horstmann, Graham-Otto's 'Lehrbuch der Chemie,' vol. i. 3, 375.

considered that it might be possible to trace some similarity between the magnetic and other properties of isomerides. The data have therefore been collected together in the above table. The values of molecular magnetic rotations have been taken from Perkin's † papers. The values of the boiling-points are those carefully determined by us. The values of r for orange incident light, except in the case of nitro-toluenes, have been taken from

† *Loc. cit.*

Krishnan's * data and the values of molecular volumes have been taken from Lossen's [21] data.

An examination of the above table shows the following significant relations :—

(1) The values of x_M for aliphatic isomerides increase in the order primary—secondary—tertiary, and, as given before, the difference between the values for tertiary and secondary is much less than that between the values for secondary and primary isomerides.

(2) In the case of aromatic isomerides the value of x_M for ortho is maximum. And the values for meta and para, like their other physical properties, are near together.

(3) In every group the isomeride having a larger value of the molecular magnetic rotation has also a larger value of the molecular magnetic susceptibility.

(4) In every group the isomeride of a higher boiling-point has got a lower magnetic susceptibility.

(5) In the case of primary, secondary, and tertiary alcohols, the one with a larger molecular volume has also a larger magnetic susceptibility, but in the case of aromatic isomerides, on the other hand, ortho having the smallest molecular volume, has got the largest magnetic susceptibility.

(6) According to Krishnan (*loc. cit.*) within the same series of compounds, increased symmetry causes more perfect polarization. In a group of isomerides, therefore, the values of the depolarization factor v can be taken as a measure of the anistropy of the molecule. And we find, in all the groups of isomerides for which the values of v are available, that the more anisotropic the molecule, the smaller its magnetic susceptibility. The values of v have also been measured for the three isomeric xylenes, and the value is least for the isomeride, which, according to all the above observations, has got maximum susceptibility. Further, the true anisotropy of the molecule is given by the value of v in the gaseous state. And we find that the above relation between x_M and v holds as well with the values of v for vapours of organic isomers, as observed by Ganesan[22] and by Rama Krishna Rao (*loc. cit.*).

* *Loc. cit.*

An explanation of the above facts will be given shortly when more data are available. But it might be pointed out here that, in the case of isomerides, not only the nature and number of the atoms are the same, but the number and nature of the valency bonds remain unaltered. The only difference that has occurred is a change in the spatial arrangement of groups of atoms constituting the molecule and its consequent effect on the orientation of molecules with respect to one another. And, therefore, in order to give a complete explanation of the influence of position isomerism on magnetic susceptibilities, it is necessary to consider the effect of changes in spatial arrangements of various groups constituting the molecule. From this standpoint, a large number of solid and liquid isomerides, including optical isomers,—are being investigated.

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X. *Note on the Potential and Attraction of Rectangular Bodies.* *By* C. E. Wright *.

§ 1. *Introduction.*

THE evaluation of the mutual potential of two extended bodies presents considerable difficulty unless the shape of the bodies is especially simple. For the needs of astronomy the case of widely-separated bodies has been discussed to an adequate degree of approximation. There are also very many elegant theorems on the attraction of ellipsoids and of nearly spherical bodies: in general these are not susceptible of simple numerical evaluation.

The case of *similarly oriented* rectangular bodies is amenable to straightforward methods, and numerical values can be obtained without excessive labour. As the results do not seem to be readily accessible, some discussion of this case is here attempted.

§ 2. *Notation and Method.*

The bodies concerned are rods, rectangular laminæ, and rectangular solids (cuboids). Since the densities of these bodies and the constant of gravitation (or force) can be supplied at will from consideration of "dimensions," these will be omitted. The coordinates of the geometric centre of one body relative to that of the other appear in the formulæ deduced. Hence it will be clear that whether attraction or repulsion is concerned, the *signs* of the component forces and couples can be determined from the configuration; and so in numerical values these signs are omitted.

The centre of the first body is taken at an origin of rectangular coordinates (O, x, y, z). The coordinates of the centre of the second body will be denoted by (ξ, η, ζ), and through this point (O') is drawn a system (O', x', y', z') parallel to (O, x, y, z) and similarly oriented. The dimensions of the bodies, in the most general case considered, are $(2a, 2b, 2c)$, $(2a', 2b', 2c')$ respectively, parallel to Ox, Oy, Oz. The value of the mutual potential,

$$V = \Sigma\Sigma \frac{mm'}{r},$$

* Communicated by the Author.

is then given by the integral

$$\int_{-a}^{+a}\int_{-a'}^{+a'}\int_{-b}^{+b}\int_{-b'}^{+b'}\int_{-c}^{+c}\int_{-c'}^{+c'} \frac{dx\,dx'\,dy\,dy'\,dz\,dz'}{\{(\xi+x'-x)^2+(\eta+y'-y)^2+(\zeta+z'-z)^2\}^{\frac{1}{2}}}.$$

This, and most of the corresponding integrals which arise later, may be simplified by a method which depends essentially on the fact that the limits of integration are constant, and which has been employed in the consideration of a mathematically similar problem (Phil. Mag., June 1929, p. 940).

Writing

$$\xi+x'-x=u, \quad \eta+y'-y=v, \quad \zeta+z'-z=w,$$

integration with respect to x' and $-x$ may each be represented by integration with respect to u, and similarly for the other pairs. With

$$\mathrm{P}^2=u^2+v^2+w^2$$

the result becomes

$$\mathrm{V}=-\int\int\int\int\int\int\frac{(du)^2(dv)^2(dw)^2}{\mathrm{P}}.$$

Disregarding sign for the moment, let this integral be represented by (112233). It will be found that all the integrals represented by omission of any number (up to five inclusive) of the digits in the above symbol will represent mutual (or simple) potentials for the cases indicated. But, further, they also yield the force components of one body on the other. To see this, in the general case take Z the force component of the first body on the second, in the direction Oz. This is given by

$$\pm\frac{\partial \mathrm{V}}{\partial\zeta}=\pm\frac{\partial}{\partial w}[\mathrm{V}],$$

provided that the differentiation takes place on the general integral, and afterwards substitution takes place for *all* the variables (x, x', y, y', z, z'). But $\dfrac{\partial \mathrm{V}}{\partial w}$ may be symbolized by (11223·), with some distinctive notation for the sixfold substitution, say $(11223\cdot)_6$.

The integral (11223·) thus admits of two interpretations:—

(*a*) Let the variables be x, x', y, y', z, so that, u, v being as before, $w=\zeta-z$. Then $\pm(11223\cdot)$ is the mutual potential of a rectangular solid and a plate in the $x'y'$ plane.

(*b*) Let x, x', y, y', z, z' all occur ($w=\zeta+z'-z$), and let substitution for all six take place. This is the case considered above.

Similar results hold for some of the other cases. as noted below.

§ 3.

This method of integration does not permit the deduction of the couple components by means of virtual work, since continuous angular change is not provided for. Direct evaluation reduces partially to integrals of the class considered above. Thus N, the component about Oz, of the couple exerted on the body with centre (ξ, η, ζ) is given by the integral of $\pm\{(\eta+y')u-(\xi+x')v\}/\mathrm{P}^3$ or of $(yu-xv)/\mathrm{P}^3$ since

$$(\eta+y'-y)u-(\xi+x'-x)v\equiv 0.$$

But taking the integrations in convenient order,

$$\int\frac{v\,dx}{\mathrm{P}^3}=-\frac{1}{\mathrm{P}},$$

and substituting in the sixfold integral gives

$$\pm\,\mathrm{N}=\int x(1233)\,dx-\int y(1233)\,dy,$$

and similarly for L and M.

§ 4.

The results for the various cases are brought up to the point at which numerical substitution may be employed. Since as many as nine parameters (a etc., a' etc., ξ etc.) may remain, such interest as the problem contains would not justify further general consideration. But a sufficient numerical view can be given when all the dimensions are the same ($a=a'=b=b'=c=c'$, except such as vanish). Let $\phi(u, v, w)$ be any integral, and write

$$\xi=2\lambda a,\quad \eta=2\mu a,\quad \zeta=2\nu a,$$

and let ϕ become $\psi(\lambda, \mu, \nu)$. Substitution for x (or x') gives then

$$\pm\{\psi(\lambda+\tfrac{1}{2}, \mu, \nu)-\psi(\lambda-\tfrac{1}{2}, \mu, \nu)\},$$

or a central difference of ψ with respect to λ. Hence a tabulation for ψ at unit intervals would lead, by differencing, to the numerical values required. In practice it is found that this method gives sufficient values for the construction of reasonably accurate diagrams.

§ 5.

When the distance between the bodies is relatively large, expansion of the integrands in ascending powers of $x'-x$ etc. may be employed as in the well-known general method. The result of integration of a term involving $(x'-x)^p$ yields a factor

$$A_{p+2} \equiv \frac{2}{(p+1)(p+2)}\{(a'+a)^{p+2}-(a'-a)^{p+2}\}$$

if p is even (including $p=0$), and zero if p is odd. For the special case of equal dimensions, the integral of $(x'-x)^p(y'-y)^q(z'-z)^r$

$$= \frac{2^{p+q+r+3}a^{p+q+r+6}}{(p+1)(p+2)(q+1)(q+2)(r+1)(r+2)}$$

or zero, the finite value requiring p, q, r all even.

§ 6. *Evaluation of the Integrals.*

(1) $$\int \frac{du}{\mathrm{P}} = \log(u+\mathrm{P}), \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

(11) $$\iint \frac{(du)^2}{\mathrm{P}} = u\log(u+\mathrm{P})-\mathrm{P}, \quad . \quad . \quad . \quad \text{(B)}$$

(12) $$\iint \frac{du\,dv}{\mathrm{P}} = v\log(u+\mathrm{P})+u\log(v+\mathrm{P}) + w\tan^{-1}\frac{w\mathrm{P}}{uv}, \quad \text{(C)}$$

(112) $$\iiint \frac{(du)^2 dv}{\mathrm{P}} = uv\log(u+\mathrm{P})+uw\tan^{-1}\frac{w\mathrm{P}}{uv} + \tfrac{1}{2}(u^2-w^2)\log(v+\mathrm{P})-\tfrac{1}{2}v\mathrm{P}, \quad \text{(D)}$$

(123) $$\iiint \frac{du\,dv\,dw}{\mathrm{P}} = \sum_{u,v,w}\left[wv\log(u+\mathrm{P}) + \tfrac{1}{2}u^2\tan^{-1}\frac{u\mathrm{P}}{vw}\right], \quad \ldots \quad (\mathrm{E})$$

(1122) $$\iiiint \frac{(du)^2(dv)^2}{\mathrm{P}} = \tfrac{1}{2}u(v^2-w^2)\log(u+\mathrm{P}) + \tfrac{1}{2}v(u^2-w^2)\log(v+\mathrm{P}) + uvw\tan^{-1}\frac{w\mathrm{P}}{uv} + \tfrac{1}{2}w^2\mathrm{P} - \tfrac{1}{6}\mathrm{P}^3, \quad (\mathrm{F})$$

(1123) $$\iiiint \frac{(dw)^2\,dv\,dw}{\mathrm{P}} = uvw\ \mathrm{og}(u+\mathrm{P}) + \tfrac{1}{2}(u^2w-\tfrac{1}{6}w^3)\log(v+\mathrm{P}) + \tfrac{1}{2}(u^2v-\tfrac{1}{6}v^3)\log(w+\mathrm{P}) + \tfrac{1}{6}u^3\tan^{-1}\frac{u\mathrm{P}}{wv} + \tfrac{1}{2}uv^2\tan^{-1}\frac{v\mathrm{P}}{uw} + \tfrac{1}{2}uw^2\tan^{-1}\frac{w\mathrm{P}}{uv}, \quad \ldots \quad (\mathrm{G})$$

(11223) $$\iiint\iint \frac{(du)^2(dv)^2\,dw}{\mathrm{P}} = \tfrac{1}{6}uw(3v^2-w^2)\log(u+\mathrm{P}) + \tfrac{1}{6}vw(3u^2-w^2)\log(v+\mathrm{P}) + \tfrac{1}{24}(6u^2v^2-u^4-v^4)\log(w+\mathrm{P}) + \tfrac{1}{6}uv^3\tan^{-1}\frac{v\mathrm{P}}{uw} + \tfrac{1}{6}vu^3\tan^{-1}\frac{u\mathrm{P}}{vw} + \tfrac{1}{2}uvw^2\tan^{-1}\frac{w\mathrm{P}}{uv} + \tfrac{1}{15}\mathrm{P}w^3 - \tfrac{1}{8}(u^2+v^2)\mathrm{P}w, \quad \ldots \quad (\mathrm{H})$$

(112233) $$\iiiint\iint \frac{(du)^2(dv)^2(dw)^2}{\mathrm{P}} = \tfrac{1}{24}\Sigma(6u^2v^2-u^4-v^4)w\log(\mathrm{P}+w) + \tfrac{1}{6}\Sigma u^3vw\tan^{-1}\frac{u\mathrm{P}}{vw} + \tfrac{1}{60}\Sigma(u^4-3u^2v^2). \quad \ldots \quad (\mathrm{K})$$

In these integrations terms arise which will clearly give zero result on substitution. Such terms have been omitted and hence cross-differentiation of the various integrals will not always give results in complete agreement ; but complete differentiation should always restore the integrand P^{-1}.

For numerical work it may be noted that (after substitution of limits) u, v, w are built up by mere addition from ξ, a, a' ; η, b, b' ; and ζ, c, c' : hence the tabulation of the integrals as functions of u, v, w will be effective. The forms which require tabulation reduce, in fact, to $\log(u+P)$ and $\tan^{-1} uP/vw$; these are symmetrical in two of the variables, and the surfaces of equal values are given, for

$$\log(u+P) = K,$$

by the confocal paraboloids of revolution

$$v^2+w^2 = e^K(e^K-2u),$$

and for the function

$$\tan^{-1} uP/vw = \beta,$$

by the quartic cones

$$u^2(u^2+v^2+w^2) = w^2v^2\tan^2\beta.$$

Both these functions also satisfy

$$\left\{\frac{\partial^2}{\partial u^2}+\frac{\partial^2}{\partial v^2}+\frac{\partial^2}{\partial w^2}\right\}\phi = 0.$$

§ 7.

Some of the results arising directly from the integrals in § 6 will now be considered in a little detail, and in the next paragraph some numerical results will be given.

(A) $\log(u+P)$; $u=\xi-x$, $v=\eta$, $\zeta=w$ gives the potential of a uniform rod at any point in space.

(B) With substitution $u=\xi+x'-x$, $v=\eta$, $w=\zeta$ gives the mutual potential of two parallel rods. The force components (always the force exerted on the second body by the first) are given numerically by values

$$X = \frac{\partial B}{\partial \xi} = \frac{\partial B}{\partial u} = (A)_{x,x'}$$

(the notation indicating substitution for x and x in the

function (A) and substitution of limits for these variables. Thus $(A)_{x,x'}$ here stands for

$$\log\left[(\xi+x'-x)+\{(\xi-x'+x)^2+\eta^2+\zeta^2\}^{\frac{1}{2}}\right]_{x=-a}^{+a}\Bigg]_{x'=-a'}^{+a'},$$

whilst for the potential of a rod, (A) stands for

$$\log\left[(\xi-x)+\{(\xi-x)^2+\eta^2+\zeta^2\}^{\frac{1}{2}}\right]_{x=-a}^{+a}$$

and so in all similar cases as indicated, § 2, end),

$$Y=\frac{\partial B}{\partial v}=\left(\frac{v}{u+P}\right)_{x,x'},\qquad Z=\left(\frac{w}{u+P}\right)_{x,x'}.$$

(C) With variables x, y this gives the potential, at any point in space, of a uniform rectangular plate; the intensity components follow in the usual way *.

If variables x, y' are used, the mutual potential of two rods at right angles is derived from the same integral, and the components of force are given by

$$X=(\pm)\log(v+P),\qquad Y=\log(u+P),$$

$$Z=\pm\frac{\partial C}{\partial w}=\pm\left[\frac{wv}{w^2+v^2}+\frac{wu}{w^2+u^2}+\tan^{-1}\frac{wP}{uv}\right].$$

(D) Substitution x, x', y gives the mutual potential of a rectangle and a rod parallel to one of its edges. The force components are

$$X=\pm(12\cdots)_3,\qquad Y=(11\cdots)_3,$$

$$Z=\pm\frac{\partial}{\partial w}(112\cdots)=\pm\left[w\log(u+P)-u\tan^{-1}\frac{wP}{uv}\right.$$

$$\left.-\frac{uvw}{v^2+w^2}-\frac{1}{2}\frac{(u^2-w^2)(2v-P)}{u^2+w^2}\right],$$

with triple substitution.

(E) Substitution x, y, z gives the potential of a rectangular solid at a point. The force components are

$$\pm(23\cdots)_3,\qquad \pm(13\cdots)_3,\qquad \pm(12\cdots)_3.$$

* When a simple potential arises from the integral, a suitable factor evidently gives the mutual potential of the body concerned (centre at *origin*) and a uniform sphere or spherical shell with centre at (ξ, η, ζ).

When the substitution is x, y, z' the mutual potential of a rectangle and a rod perpendicular to its plane arises. The force components are as before, except for the substitution.

(F) The substitution is for (x, y, x', y'), and gives the mutual potential of two rectangular plates in parallel planes. The force components are

$$(122\cdots)_4, \quad (112\cdots)_4, \quad \text{and} \quad \pm\frac{\partial F}{\partial w}$$

$$= \pm\left[\frac{1}{2}\frac{uw(v^2-w^2)}{P(u+P)} + \frac{1}{2}\frac{vw}{P}\cdot\frac{u^2-w^2}{v+P}\right.$$

$$-uw\log(u+P) - vw\log(v+P)$$

$$\left. + \frac{u^2v^2w}{P}\left\{\frac{1}{u^2+w^2} + \frac{1}{v^2+w^2}\right\} + \frac{1}{2}\frac{w(P^2+w^2)}{P}\right].$$

(G) Substitution x, x', y, z gives the mutual potential of a solid and a rod parallel to one of its edges.

Substitutions (x, x', y', z) or (x, x', y, z') give mutual potentials of rectangular laminæ with planes at right angles. The force components are derivable from

$$(123\cdots)_4, \quad (113\cdots)_4, \quad (112\cdots)_4,$$

with corresponding substitution in the several cases.

(H) Substitution x, x', y, y' and (z or z') gives mutual potential of rectangular solid and lamina whose plane is parallel to a face of the solid. The force components are derived from

$$(1223\cdot\cdot)_5, \quad (1123\cdot\cdot)_5, \quad (1122\cdot\cdot)_5,$$

with the proper substitutions.

(K) The mutual potential of similarly oriented rectangular solids. The force and couple components are indicated in §§ 2, 3 respectively.

§ 8.

Short tables of the functions $\log_e\{\lambda+(\lambda^2+\mu^2)^2\}$ (Table I.) and $\tan^{-1}\frac{(1+\alpha^2+\beta^2)^{\frac{1}{2}}}{\alpha\beta}$ (Table II.) are included for use in numerical evaluations. As examples, the case of equal parallel rods is considered in some detail.

TABLE I.

Values of $10^7 \log_e \{\lambda + (\lambda^2 + \mu^2)^{\frac{1}{2}}\}$.

λ.	$\mu=1$.	$\mu=2$.	$\mu=3$.	$\mu=4$.
0	0	6931472	10986122	13862943
	8813736	11743590	14260624	16337608
	14436354	15745207	17237573	18675061
	18184464	18879103	19799858	20794415
	20947125	21367826	21972245	22676678
5	23124382	23403782	23824079	24338873
	24917797	25115935	25422476	25810575
	26441206	26588675	26821012	27121920
	27764722	27878596	28060236	28299297
	28934439	29024948	29170586	29364522
10	29982228	30055854	30175086	30335254
	30931021	30992062	31091391	31225718
	31797853	31849269	31933247	32047407
	32595724	32639617	32711517	32809664
	33334774	33372678	33434912	33520147
15	34023065	34056123	34110505	34185188
	34667109	34696193	34744112	34810068

λ.	$\mu=5$.	$\mu=6$.	$\mu=7$.	$\mu=8$.
0	16094378	17916903	19459101	20794415
	18081279	19576639	20882857	22041182
	19994731	21192095	22278738	23269079
	21782627	22729711	23623408	24461660
	23421062	24169045	24900813	25606533
5	24908114	25502455	26102407	26695851
	26254109	26731330	27225803	27725886
	27474198	27862168	28272836	28696102
	28584211	28903717	29247809	29608150
	29598785	29865226	30156208	30465011
10	30530733	30755550	31003874	31270434
	31390983	31582746	31796526	32028061
	32188757	32353948	32539511	32742046
	32931809	33075392	33237697	33416007
	33626667	33752483	33895455	34053392
15	34278842	34389900	34516668	34657358
	34893013	34991708	35104776	35230769

TABLE I. (*contd.*).

Values of $10^7 \log_e \{\lambda + (\lambda^3 + \mu^2)^{\frac{1}{2}}\}$.

λ.	$\mu=9$.	$\mu=10$.	$\mu=11$.	$\mu=12$.
0	21972245	23025851	23978952	24849066
	23081082	24024191	24886794	25681437
	24176572	25012751	25787262	26508111
	25246746	25982580	26673499	27323730
	26282026	26926203	27539599	28123567
5	27275671	27837968	28380864	28903717
	28223696	28714099	29193890	29661184
	29124459	29552515	29976506	30393874
	29978097	30352532	30727613	31100516
	30785981	31114519	31446981	31780537
10	31550249	31839586	32135040	32433927
	32273465	32529319	32792687	33061105
	32958367	33185581	33421130	33662801
	33607706	33810360	34021763	34239956
	34224144	34405670	34596075	34793640
15	34810201	34973482	35145579	35324995
	35368219	35515683	35671773	35835188

λ.	$\mu=13$.	$\mu=14$.	$\mu=15$.	$\mu=16$.
0	25649493	26390572	27080501	27725702
	26417967	27104252	27746675	28350480
	27181949	27814328	28409915	28972653
	27937178	28517360	29067402	29590070
	28679823	29210204	29716533	30200551
5	29406627	29890131	30355002	30802137
	30114990	30554880	30980854	31393132
	30802949	31202690	31592392	31972127
	31469215	31832284	32188757	32538004
	32113026	32442829	32768750	33089927
10	32734101	33033878	33331952	33627323
	33332533	33605313	33878105	34149847
	33908709	34157275	34407183	34657358
	34463228	34690108	35218222	35149880
	34996834	35204308	35414890	35627530
15	35510367	35700475	35894236	36090705
	36004723	36179280	36357873	36539622

Table II.

Values of $\tan^{-1}\frac{(1+\alpha^2+\beta^2)^{\frac{1}{2}}}{\alpha\beta}$.

β \ α.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
1.	1·0471976	0·8860770	0·8354818	0·8148264	0·8046356	0·7989147	0·7953999	0·7930922	0·7914971	0·7903181
2.		0·6435029	0·5578897	0·5201954	0·5010937	0·4904520	0·4855991	0·4788602	0·4756895	0·4735681
3.			0·4510270	0·4078074	0·3756724	0·3652004	0·3506512	0·3441743	0·3396216	0·3363201
4.				0·3447025	0·3132914	0·2945195	0·2823895	0·2741670	0·2683540	0·2641022
5.					0·2782442	0·2566167	0·2425620	0·2328631	0·2259425	0·2208375
6.						0·2330209	0·2173129	0·2063900	0·1985119	0·1926601
7.							0·2003347	0·1884180	0·1797107	0·1732094
8.								0·1755413	0·1662717	0·1592080
9.									0·1563331	0·1486924
10.										0·1408384

From the integral B, with $u=\xi+x'-x$ and limits $-a$ to $+a$ for x and x', together with the substitution $w=\zeta=0$ (evidently permissible in this case), the following values arise : —

Mutual Potential.

$$\epsilon V = 2a\Delta^2\left[\lambda \log_e\{\lambda+(\lambda^2+\mu^2)^{\frac{1}{2}}\}-(\lambda^2+\mu^2)^{\frac{1}{2}}\right].$$

Force.

$$\epsilon X = \Delta^2 \log_e\{\lambda+(\lambda^2+\mu^2)^{\frac{1}{2}}\},$$

$$\epsilon Y = \Delta^2 \frac{1}{\lambda+(\lambda^2+\mu^2)^{\frac{1}{2}}} = \frac{1}{\mu}\Delta^2(\lambda^2+\mu^2)^{\frac{1}{2}}.$$

Couple.

$$\epsilon N = 2a^2\left[\int_{\mu}^{\lambda}\Delta^2(\lambda^2+\mu^2)^{\frac{1}{2}} - \Delta^2\log_e\{\lambda+(\lambda^2+\mu^2)^{\frac{1}{2}}\}\right].$$

Here $\epsilon=\pm1$, chosen to make the values positive in general ; and the differences refer to λ only.

Tables for the potential and force components are given below.

TABLE III.

Values of

$$10^7\epsilon V/2a \equiv 10^7\Delta_\lambda{}^2\left[\lambda \log_e\{\lambda+(\lambda^2+\mu^2)^{\frac{1}{2}}\}-(\lambda^2+\mu^2)^{\frac{1}{2}}\right].$$

λ.	$\mu=0$.	$\mu=1$.	$\mu=2$.	$\mu=3$.
0	∞	9343200	4902876	3303450
	∞	7168828	4440323	3143839
	5232478	4578161	3552120	2771748
	3397984	3208242	2792795	2362279
	2526712	2447442	2249170	2006083
5	2009410	1973171	1865477	1720045
	1682761	1651165	1586774	1434595
	1429324	1418828	1387721	1315962
	1253272	1243466	1215403	1172595
	1113420	1106523	1086631	1055758
10	1001657	996673	982070	959112
	910358	906672	895561	878074
	834297	831405	822886	809248
	769982	767710	760899	750192
	714908	713079	707870	698956
15	664210	665675	661199	654163

TABLE III. (*contd.*).

Values of

$$10^7\epsilon V/2a \equiv 10^7\Delta_\lambda{}^2[\lambda \log_e\{\lambda+(\lambda^2+\mu^2)^{\frac{1}{2}}\}-(\lambda^2+\mu^2)^{\frac{1}{2}}].$$

λ.	μ=4.	μ=5.	μ=6.	μ=7.
0	2487218	1993408	1662840	1426156
	2415658	1955646	1640609	1412019
	2232373	1853818	1578834	1371918
	2000342	1714096	1489603	1312066
	1770028	1562242	1386564	1239925
5	1563348	1415379	1280764	1162484
	1391138	1281711	1179177	1084839
	1241355	1163768	1085440	1010581
	1119669	1061143	1000755	941204
	1016661	972280	935206	877540
10	929531	895255	848137	820099
	855224	828309	798629	766600
	791270	769819	745856	720584
	735784	718467	698827	687644
	687280	673079	656841	639172
15	644577	632819	619441	604404

λ.	μ=8.	μ=9.	μ=10.	μ=11.
0	1248380	1109972	999170	908466
	1238835	1103237	994242	904757
	1211458	1083741	979886	893888
	1169572	1053409	947278	876614
	1117561	1014910	928084	854020
5	1059841	971056	894190	827376
	1000068	924448	857378	797956
	940919	877128	819229	766910
	884179	830618	780938	735221
	831664	785864	743413	703662
10	779409	743519	707245	672864
	736424	703832	672828	642937
	693680	666898	640371	614412
	655402	632660	609873	587356
	620420	601061	581401	561764
15	588459	571836	554848	537736

Values of TABLE III. (*contd.*).

$$10^7\epsilon V/2a \equiv 10^7\Delta_\lambda{}^2\left[\lambda \log_e\{\lambda+(\lambda^2+\mu^2)^{\frac{1}{2}}\}-(\lambda^2+\mu^2)^{\frac{1}{2}}\right].$$

λ.	μ=12.	μ=13.	μ=14.	μ=15.	μ=16.
0	832852	768852	713984	666420	624120
	829989	766596	712172	664948	623581
	821570	759944	706833	660592	619987
	808091	749235	698180	653513	614122
	790282	734971	686596	643978	606185
5	769017	717792	672510	632311	596418
	745213	698206	656399	618057	585102
	719746	677250	638791	605656	572517
	693357	655073	620102	587371	558954
	666687	632458	600764	571626	544711
10	640230	609720	581319	554684	529970
	614363	587265	561676	537619	515015
	589347	565304	542355	520705	500006
	565320	543190	523480	503804	484482
	542424	525086	505126	487416	471604
15	520683	503095	486937	471449	455380

TABLE IV.

Values of $10^7\epsilon X \equiv 10^7\Delta_\lambda{}^2 \log_e\{\lambda+(\lambda^2\pm\mu^2)\}$.

λ.	μ=0.	μ=1.	μ=2.	μ=3.
0		0	0	0
	∞	3191118	810500	297553
	2876820	1874508	867720	414664
	1177830	985449	645174	389898
	645384	585404	452767	320553
5	408223	383842	323803	253437
	281708	270006	239412	199861
	206192	199893	182821	159312
	157483	153799	143568	128874
	124226	121928	115446	105850
10	100504	98996	94698	88195
	82987	81961	79001	74449
	69687	68961	66859	63586
	59347	58821	57287	54875
	51152	50759	49614	47802
15	44542	44247	43375	41986

TABLE IV. (*contd.*).

Values of $10^7\epsilon X \equiv 10^7\Delta_\lambda{}^2 \log_e\{\lambda+(\lambda^2\pm\mu^2)\}$.

λ.	$\mu=4$.	$\mu=5$.	$\mu=6$.	$\mu=7$.
0	0	0	0	0
	137312	73449	44280	27875
	218099	125556	77838	51211
	237091	149461	98284	67265
	220068	151383	105924	75811
5	190493	141057	104535	78198
	160357	125906	98027	76363
	133968	110076	89309	72060
	112152	95439	80030	66574
	94493	82626	71185	60733
10	80268	71698	63128	55014
	68775	62476	55994	49667
	59432	54722	49758	44529
	51774	48194	44353	40968
	45442	42680	39674	36275
15	40161	38010	35609	33105

λ.	$\mu=8$.	$\mu=9$.	$\mu=10$.	$\mu=11$.
0	0	0	0	0
	18870	13347	9780	7374
	35316	25316	18731	14231
	47708	34894	26206	20137
	55555	41635	31858	25835
5	59283	45620	35634	27239
	59820	47262	37715	30410
	58166	47125	38399	31509
	55189	45754	38030	31739
	51526	43616	36920	31309
10	47617	41052	35334	30412
	43732	38314	33471	29204
	40024	35563	31483	27810
	36576	32901	29469	26319
	33429	30381	27498	24808
15	30546	28039	25611	23310

TABLE IV. (*contd.*).

Values of $10^7 \epsilon X \equiv 10^7 \Delta_\lambda{}^2 \log_e\{\lambda + (\lambda^2+\mu^2)\}$.

λ.	μ=12.	μ=13.	μ=14.	μ=15.	μ=16.
0	0	0	0	0	0
	5697	4492	3604	2934	2605
	11055	8753	7044	5753	4756
	15782	12584	10188	8356	6936
	19687	15841	12917	10662	8895
5	22683	18441	15178	12617	10591
	24777	20404	16939	14314	12000
	26048	21693	18216	15173	13118
	26621	22455	19052	16372	13954
	26631	22736	19490	16791	14537
10	26212	22643	19617	17049	14872
	25482	22256	19473	17075	15013
	24541	21657	19129	16917	14989
	23471	20913	18633	16615	14872
	22329	20073	18033	16197	14475
15	21162	19177	17392	15709	14258

TABLE V.

Values of $10^7 \epsilon Y \equiv \frac{10^7}{\mu} \Delta_\lambda{}^2 (\lambda^2+\mu^2)^{\frac{1}{2}}$.

λ.	μ=1.	μ=2.	μ=3.	μ=4.
0	8284272	2360680	1081851	614528
	4076408	1781456	936053	564812
	1043553	923826	646053	447084
	346182	447303	400900	322476
	150860	232221	245309	223539
5	78291	131809	154334	154271
	45623	80821	101057	107942
	28846	52734	68871	77148
	19375	36159	48662	56429
	13631	25807	35481	42215
10	9949	19032	26581	32246
	7482	14422	20383	25101
	5766	11181	15949	19873
	4538	8840	12699	15974
	3636	7106	10268	13014
15	2955	5796	8416	10732

TABLE V. (*contd.*).

Values of $10^7 \epsilon Y \equiv \frac{10^7}{\mu} \Delta^2 (\lambda^2 + \mu^2)^{\frac{1}{2}}$.

λ.	$\mu=5$.	$\mu=6$.	$\mu=7$.	$\mu=8$.
0	396078	275875	203051	155644
	374252	265051	197106	152120
	319284	236426	180887	142299
	252770	198750	158316	128095
	191543	160414	133690	111801
5	142477	126474	110217	95387
	105787	98719	89616	80159
	79160	76987	72429	66771
	59986	60331	58511	55404
	46122	47660	47418	45960
10	35993	38017	38640	38210
	28496	30639	31700	31891
	22869	24949	26200	26747
	18584	20520	21819	22557
	15278	17039	18310	19133
15	12693	14275	15477	16324

λ.	$\mu=9$.	$\mu=10$.	$\mu=11$.	$\mu=12$.
0	123078	99751	82475	69324
	120860	98288	81471	68613
	114588	94104	78578	66551
	105263	87756	74119	63335
	94164	79987	68546	59246
5	82502	71554	62338	54600
	71196	63088	55929	49790
	60822	55041	49659	44938
	51652	47683	43758	40027
	43749	41136	38362	35587
10	37049	35422	33529	31518
	31426	30498	29264	27851
	26732	26289	25540	24584
	22823	22711	22311	21800
	19567	19675	19522	19167
15	16850	17100	17119	16953

TABLE V. (*contd.*).

Values of $10^7 \epsilon Y = \frac{10^7}{\mu} \Delta_\lambda^3 (\lambda^2 + \mu^2)^{\frac{1}{2}}$.

λ.	$\mu=13$.	$\mu=14$.	$\mu=15$.	$\mu=16$.
0	59084	50955	44395	39024
	58567	50570	44102	38798
	57058	49442	43242	38131
	54684	47652	41869	37061
	51624	45322	40065	35644
5	48088	42592	37928	33951
	44284	39609	35563	32056
	40394	36507	33069	30033
	36566	33401	30534	27951
	32908	30380	28030	25867
10	29489	27507	27612	23827
	26348	24823	23319	21867
	23501	22349	21169	20010
	20944	20095	19194	18272
	18664	18056	17378	16661
15	16642	16223	15727	15178

§ 9. *Extensions to other Inverse Power Laws.*

Let I be any integral in which w does not occur as a variable of integration. Replace w^2 by α. Then $\underset{\alpha \to 0}{\mathrm{Lt}} \left(\frac{\partial}{\partial \alpha}\right)^s \mathrm{I}$ gives the result corresponding to I in the case of attraction proportional to $r^{-(2+2s)}$. Deduction for odd powers of r would require the initial integration of $(u^2+v^2+\alpha)^{-1}$ or for the law r^{-1}, of $\log(u^2+v^2+\alpha)$. The most general case of the kind requires the evaluation of

$$\iiint\iiint \mathrm{Q}\,(du)^2\,(dv)^2(dw)^2$$

with the values

$$\mathrm{Q} = (u^2+v^2+w^2+\alpha)^{-\frac{1}{2}},$$

$$(u^2+v^2+w^2+\alpha)^{-1}, \quad \text{and} \quad \log(u^2+v^2+w^2+\alpha)$$

with subsequent differentiations with respect to α.

Blackheath.
18 Dec., 1929.

XI. *The Isotope Effect in Neon Lines.* *By* Elfed Thomas, *B.Sc., and* Prof. E. J. Evans, *D.Sc., University College of Swansea* *.

THE isotope effect in the line spectra of some elements has been examined by Aronberg †, Harkins ‡, Merton §, Perete-Montamat ‖, McLennan and Ainslie ¶, and by Schüler and Wurm **. During the past three years investigations have been carried out at Swansea on the structure and width of spectrum lines, and the present work on the neon lines was submitted to Prof. A. Fowler, who informed us of the important investigation which had been carried out by Nagaoka and Mishima †† on the same problem. The results of the present investigation confirm those of Nagaoka and Mishima, who found that every strong neon line was accompanied by a weaker companion situated on the lower wave-length side of the strong line. When, however, the experimental values of the separations of the lines are compared, it is seen that the agreement is not complete.

In the present experiments the source of light was an ordinary spectrum tube containing neon, which was connected to the secondary terminals of an induction coil. An approximately parallel beam of light from the capillary portion of the tube was directed towards the Fabry-Perot interferometer by means of a lens, and the fringes focussed on the slit of a Hilger constant deviation spectroscope. When the spectrum tube was immersed in liquid air, it was found that the bright circular fringes were accompanied by much fainter ones, which had slightly lower wave-lengths than the bright fringes. The distances apart between the faint and bright fringes could not be measured accurately with the micrometer eyepiece at our disposal, and it was therefore decided to photograph the fringes. Various exposures were

* Communicated by Prof. E. J. Evans.

† Aronberg, Proc. Nat. Acad. Sci. iii. p. 710 (1917). Astro. Journ. xlvii. p. 96 (1918).

‡ Aronberg and Harkins, Journ. Am. Chem. Soc. xlii. p. 1328 (1920).

§ Merton, Proc. Roy. Soc. xcvi. p. 388 (1920); xcix. p. 87 (1921); c p. 84 (1921).

‖ Perrete-Montamat, Thèsis (Paris, 1928).

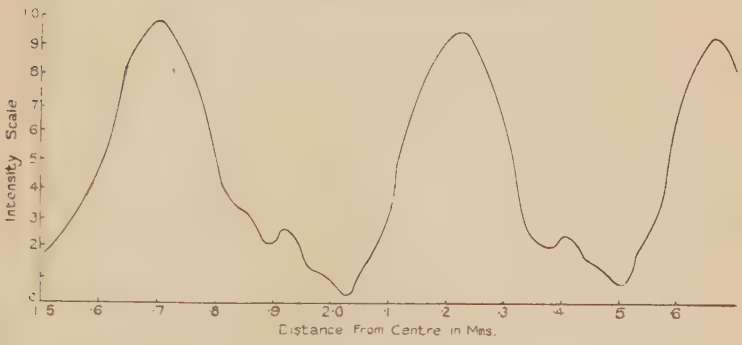
¶ McLennan and Ainslie, Proy. Roy. Soc. ci. p. 342 (1922).

** Schüler and Wurm, *Naturwiss.* xv. p 971 (1927).

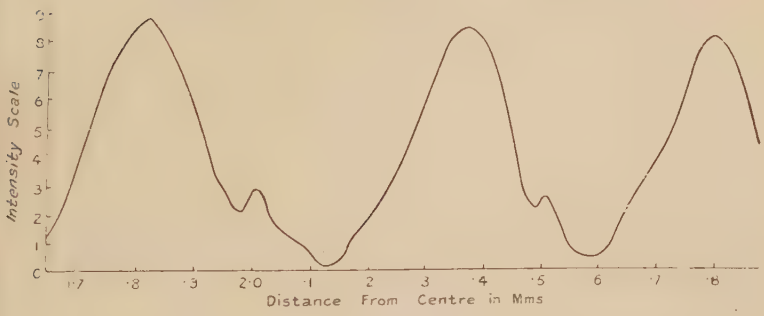
†† Nagaoka and Mishima, 'Proceedings of the Imperial Academy,' v. No. 5 (1929).

given ranging from 0·5 to 20 minutes, the longer exposures in order to bring out the faint companions of the weak neon lines. The intensity of the faint companion according to eye estimation, is from a fifth to a tenth that of its bright companion, but the relative intensity on the photographic plates depends on the exposure and on the intensity of

Curve I.—λ 6717·22 ; $e = 3{\cdot}0$ cm.



Curve II.—λ 6163·73 ; $e = 2{\cdot}5$ cm.

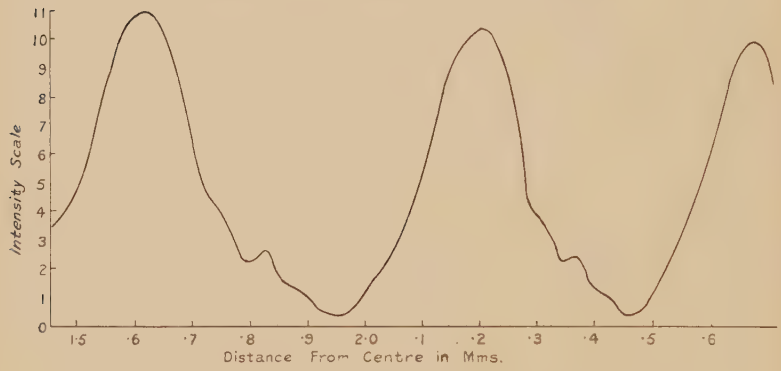


the neon line examined. The intensity distribution across the fringes was measured by means of a Cambridge microphotometer. Typical examples of the measurements are given in Curves I., II., III. and IV., which show the intensity distribution across the fringes of the 6717, 6164, 6030, and 5882 neon lines. These curves show the presence of the faint companions whose intensities are approximately about one-fourth that of their brighter companions.

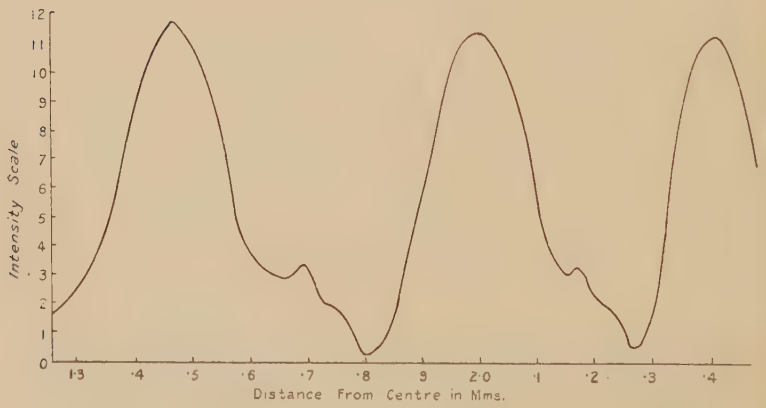
Let e = distance between the plates of the interferometer. Then path difference for rays passing through normally = $2e$. Let rays inclined at an angle θ_1 produce a ring of order m_1. Then

$$\frac{2e}{\lambda}\cos\theta_1 = m_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Curve III.—λ 6030·2 ; e = 2·5 cm.



Curve IV.—λ 5882·06 ; e = 3·0 cm.



The next ring further out from the centre will be represented by

$$\frac{2e}{\lambda}\cos\theta_2 = m_1 - 1, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\frac{2e}{\lambda}\cos\theta_f = m_1 - f, \quad \ldots\ldots \quad (3)$$

where f is a fraction less than unity.

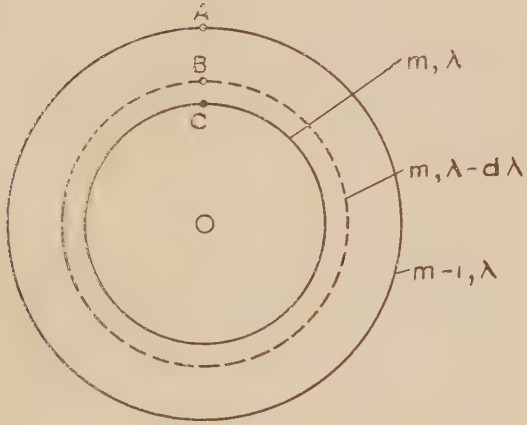
From equations (1), (2), and (3),

$$\frac{2e}{\lambda}(\cos\theta_1 - \cos\theta_2) = 1$$

and

$$\frac{2e}{\lambda}(\cos\theta_1 - \cos\theta_f) = f.$$

Fig. 1.



Expanding $\cos\theta$ and neglecting higher power than θ^2, it can be shown that

$$f = \frac{\theta_f - \theta_1}{\theta_2 - \theta_1} \cdot \frac{\theta_f + \theta_1}{\theta_2 + \theta_1}.$$

In fig. 1 let A and C represent the mth and $(m-1)$th order fringes of the stronger component λ, and let B represent the mth order of the faint component $\lambda - d\lambda$. The fraction

$$f = \frac{OB - OC}{OA - OC} \cdot \frac{OB + OC}{OA + OC}$$

$$= \frac{BC}{AC} \cdot \frac{OB + OC}{OA + OC}.$$

Now

$$m(\lambda - d\lambda) = (m-f)\lambda$$

and

$$d\lambda = \frac{f}{m} \cdot \lambda,$$

where m is very nearly equal to $\frac{2e}{\lambda}$. Therefore

$$d\lambda = \frac{f\lambda^2}{2e}$$

and

$$\frac{d\nu}{\nu} = \frac{f\lambda}{2e} \quad \text{where} \quad \nu = \frac{1}{\lambda}.$$

In this manner the separation $d\lambda$ of the faint component from its brighter companion was calculated for about twenty neon lines in the visible spectrum, and the results are given in Table I. The values of $d\lambda$ obtained by Nagaoka and Mishima are shown in column VII. of this table.

Experimental Results.

Table I. includes all the strong neon lines in the region of the spectrum investigated, and it is seen that every strong line is accompanied by a fainter companion. In addition, the value of $\frac{d\nu}{\nu}$ for the lines belonging to each Paschen series is constant within experimental error. The mean values of $\frac{d\nu}{\nu} \times 10^8$ for the series $1s_2 - 2p_m$, $1s_3 - 2p_m$, $1s_4 - 2p_m$, and $1s_5 - 2p_m$ are 437, 367, 367, and 370 respectively, and are practically constant for the last three series. An examination of the table shows that the values of $d\lambda$ obtained in the present experiments are for the first series about 15 per cent. lower on the average than those given by Nagaoka and Mishima, and for the last three series about 10 per cent. higher.

Neon, which has an atomic weight of 20·20, has been shown by Aston to consist of a mixture of two isotopes of atomic weights 20·0 and 22·0 in the ratio of 9 : 1. For an atom consisting of a nucleus with one electron theory shows that $\nu \propto \frac{Mm}{M+m}$ where M is the mass of the nucleus of the

atom, and m the mass of the electron. It therefore follows that the wave-lengths of the spectrum lines emitted by Ne(22) should be lower than those emitted by Ne(20),

TABLE I.

Series (Pashen).	Wave-length of line. λ.	Distance apart of mirrors. e cm.	Fraction f.	$\frac{d\nu}{\nu}\times10^8$.	$d\lambda$ in Å.U.	$d\lambda$ in Å.U. Nagaoka and Mishima.
$1s_2-2p_1$	5852	2·5	0·382	447	−0·0261	−0·0279
		3·0	0·456	445	−0·0259	
$1s_2-2p_2$	6599	2·5	0·329	434	−0·0286	−0·0341
		3·0	0·396	436	−0·0287	
$1s_2-2p_4$	6678	2·5	0·325	434	−0·0289	−0·0342
		3·0	0·392	436	−0·0290	
$1s_2-2p_5$	6717	2·5	0·324	435	−0·0292	−0·0361
		3·0	0·390	436	−0·0293	
$1s_2-2p_6$	6930	3·0	0·376	434	−0·0301	
$1s_3-2p_2$	6164	3·5	0·414	364	−0·0224	−0·0197
		2·5	0·298	367	−0·0226	
$1s_3-2p_5$	6266	3·5	0·407	364	−0·0228	−0·020
		3·0	0·358	373	−0·0233	
$1s_3-2p_7$	6533	3·5	0·392	366	−0·0239	−0·0218
$1s_4-2p_2$	6030	2·5	0·301	363	−0·0219	−0·0207
$1s_4-2p_3$	6074	3·0	0·358	363	−0·0220	−0·0213
$1s_4-2p_4$	6096	3·0	0·357	363	−0·0221	−0·0208
$1s_4-2p_6$	6305	3·0	0·351	369	−0·0233	−0·0205
$1s_4-2p_7$	6383	3·0	0·350	372	−0·0238	−0·0216
$1s_4-2p_8$	6507	3·0	0·344	373	−0·0243	−0·0230
$1s_5-2p_1$	5882	3·5	0·436	367	−0·0215	−0·0197
$1s_5-2p_4$	5945	3·5	0·430	365	−0·0217	−0·0198
$1s_5-2p_5$	5976	3·5	0·434	371	−0·0221	−0·0202
$1s_5-2p_6$	6143	2·5	0·307	377	−0·0232	−0·0208
		3·0	0·369	377	−0·0232	
$1s_5-2p_7$	6217	3·5	0·414	368	−0·0229	−0·0209
$1s_5-2p_8$	6334	2·5	0·291	369	−0·0234	−0·0212
		3·0	0·351	371	−0·0235	
$1s_5-2p_9$	6402	3·0	0·350	373	−0·0239	−0·0217
$1s_5-2p_{10}$	7032	3·5	0·368	370	−0·0260	−0·0254

and, in addition, it is to be expected from the composition of ordinary neon, that the Ne(22) lines should be faint as compared with the Ne(20) lines. The faint lines measured

in the present experiments satisfy both these conditions, but the value of $\frac{d\nu}{\nu}$ found experimentally is greater than that calculated from the above formula. Let ν be the wave-number of a particular line for Ne(20) having a nuclear mass M, and ν_1 the wave-number of the corresponding line for Ne(22) of nuclear mass M_1, then

$$\frac{\nu_1-\nu}{\nu}=\frac{d\nu}{\nu}=\frac{m(M_1-M)}{M(M_1+m)}=\text{constant}.$$

Putting into the equation the values of m, M, and M_1, it is found that $\frac{d\nu}{\nu}=247{\cdot}4\times10^{-8}$. The mean values of $\frac{d\nu}{\nu}$ determined experimentally are 437×10^{-8} for the series $1s_2-2p_m$, and 368×10^{-8} for the series $1s_3-2p_m$, $1s_4-2p_m$, $1s_5-2p_m$. The simple theory, however, does not apply to atoms possessing more than one electron.

The authors wish to thank Prof. A. Fowler, F.R.S., for the kind interest he has taken in this investigation.

XII. *Distribution of Electric Forces in Spaces traversed by Electrons.* *By* E. W. B. Gill, *B.Sc., M.A., Fellow of Merton College, Oxford* *.

1. In the past ten years considerable use has been made of the so called "force free" spaces in measurements of critical potentials of gases. In these experiments a stream of electrons moves from a hot filament F to a grid G_1, which is kept at a potential V above the filament. The grid G_1 is close to the filament, so most of the electrons do not collide with molecules of gas in passing from F to G_1. After passing through G_1 the electrons move in a large space between G_1 and another electrode or grid G_2 which is at the same potential as G_1. The experiments are interpreted on the hypothesis that the electrons between G_1 and G_2 move with constant velocity, except in so far as they collide with gas molecules; and the arrangement is thus supposed to enhance the effects of electrons moving with the velocity corresponding to the potential V.

* Communicated by Professor Townsend, F.R.S.

A typical example of this method occurs in the investigations made by Horton and Davies* of the critical potentials of neon. The electrons passed through a hole in an electrode G_1 and were received on another electrode G_2, 1·5 cm. from G_1. Both these electrodes were at the same potential V relative to the filament. The discharge was prevented from spreading laterally by a magnetic field, and spectroscopic and electrical observations were made on the gas between the two electrodes.

The authors say "For the purpose of determining the limiting electron velocity required to produce the particular lines in the spectrum it was necessary that the bombarding electrons should suffer no change of velocity throughout the space viewed by the spectroscope except such changes as result from collisions. To secure this condition the grid and anode were maintained at the same potential." While in another paper† they say "Since there is no potential difference between the gauges the detection of ionization depends upon the diffusion of positive ions out of this space." The minimum electron velocity they observed for a glow was about 20 volts.

It is quite clear that the authors regarded the electric force in the space between the electrodes G_1 and G_2 as being zero or negligible.

The same underlying idea is present in experiments of Franck and Hertz in which electrons entered a large metal box with gauze sides through which they diffused, and also in experiments where the electrons were projected into a large space between two grids differing in potential by a small fraction of a volt. Although the experiments quoted were made some years ago the "force free" space is still in use as a recent letter to 'Nature' indicates ‡.

2. It does not seem that sufficient consideration has been given to the effect of the space charge in the "force free space." When there is no current traversing the space between G_1 and G_2 the potential at any point is the same as at the boundary, but when electrons enter the space this is no longer the case; and as the effect of this charge has not been completely investigated it is of interest to consider to what extent the field is disturbed under the simplest conditions. The actual field depends on the current and can be calculated quite easily for plane parallel electrodes if the electrons are

* Phil. Mag., June 1921, p. 921.
† Phil. Mag., May 1920, p. 596.
‡ 'Nature,' March 22, p. 460 (1930).

moving in a vacuum or through a gas at such a low pressure that collisions are rare.

3. The calculation of the electric field due to the distribution of electrons is similar to the well-known theory of Langmuir and Child.

Let the potential of the filament be zero and let the two grids be at V. The effect of the negative charge on the electrons is to reduce the potentials in the space between the grids to values less than V. If the grids are parallel planes whose area is large compared with the distance between them, the equipotential surfaces will be planes parallel to the grids.

Fig. 1.

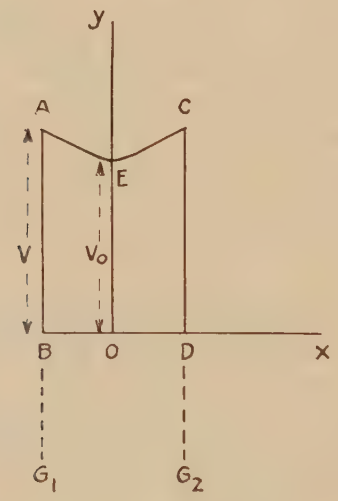


Fig. 1 represents the distribution of potential along a line normal to the grids; AB and CD are equal to V the grid potentials, BD is the distance between them, and EO the minimum potential V_0 in the space between them.

Let v be the potential at a plane distant x from the plane OE where the potential is a minimum, and let the electrons move across the space between the grids from left to right in fig. 1.

Let n be the number of electrons per cu. cm., and u the velocity of the electrons at the plane x; the direction of motion being perpendicular to the planes.

And let i be the current per sq. cm. of the plane x, e and m the charge and mass of an electron.

The quantities v, n, and u are functions of x, but in the steady motion which is considered i is a constant independent of x.

The kinetic energy of the electron is

$$\tfrac{1}{2}mu^2 = ev, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

also the current i is

$$i = neu, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

while the potential v is given by

$$\frac{d^2v}{dx^2} = 4\pi ne, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

whence

$$\frac{d^2v}{dx^2} = \frac{a}{\sqrt{v}} \text{ where } a = 4\pi i\sqrt{\frac{m}{2e}}.$$

Integrating this equation gives

$$\left(\frac{dv}{dx}\right)^2 = 4a(\sqrt{v} - \sqrt{V_0}), \quad . \quad . \quad . \quad . \quad (4)$$

since V_0 is the minimum value of v.

A second integration gives, since $v = V_0$ when $x = 0$,

$$\sqrt{\sqrt{v} - \sqrt{V_0}}\{\sqrt{v} + 2\sqrt{V_0}\} = \tfrac{3}{2}\sqrt{a}x. \quad . \quad . \quad (5)$$

If $OD = d$, then when $x = d$, $v = V$, so that the following equation for V_0 is obtained from equation (5):

$$\tfrac{9}{4}ad^2 = (\sqrt{V} - \sqrt{V_0})(\sqrt{V} + 2\sqrt{V_0})^2 \quad . \quad . \quad (6)$$

Replacing a by its numerical value the following expression is obtained for the current:

$$i = \frac{2{\cdot}33 \times 10^{-6}(\sqrt{V} - \sqrt{V_0})(\sqrt{V} + 2\sqrt{V_0})^2}{d^2}, \quad (7)$$

i being in amperes per sq. cm., V and V_0 in volts, and d in cm.

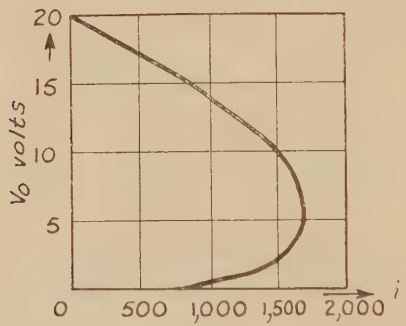
The consideration that $v = V$ at both grids proves that $OB = OD$, so that O is midway between the grids and the distribution curve is symmetrical about OE. Equation (7) thus gives the potential V_0 at the middle point of a "force free space" of length $2d$ across which a current i flows, the electrodes being at a potential V above the filament. Equation (5) gives the actual distribution of field.

4. The effect of the space-charge is seen most simply by tabulating the currents which give various values of V_0 for

some assigned value of V. Fig. 2 gives the values of the potentials V_0 midway between two grids, one centimetre apart, each at a potential of 20 volts above the filament for different currents i per sq. cm.

It will be observed that there are quite large effects due to very small currents. Thus it only requires 180 microamps. per sq. cm. to cause a drop of one volt in the "force free space," while about 500 microamps. gives a drop of 3 volts, and so on. A further interesting result is that if the current exceed a certain value (830 microamps. per sq. cm. in this case) there are two possible distributions of potential. For example, one milliamp. per sq. cm. may cause the potential at the middle to drop to either 13·7 or ·4 volts. (The possibility

Fig. 2.



Potential V_0 midway between 2 grids 1 cm. apart each at 20 volts, above the filament for different currents, i.
(i current in microamps per sq. cm.)

of two alternative distributions is not confined to gas free spaces, as they can be obtained experimentally in cases where a discharge passes through a gas at low pressure in which positive ions produced by collision are also present.) The maximum current which can traverse the space is just under 1·7 milliamps. per sq. cm., and this reduces the potential at the middle to 5 volts.

It is easily seen from equation (7) that for a given current the distortion of the field increases if either the grid potentials are reduced or the distance between the grids is increased.

5. The preceding theory only applies rigidly to large electrodes and to currents distributed uniformly over the surface, in which cases the electrons move normally to the

electrodes and there is no electric force perpendicular to their motion. In general it is impossible to calculate the effect of the space-charge, but the preceding investigation indicates approximately the effect in many experiments. Very similar calculations made by Langmuir for infinite electrodes have been found to be in good agreement with measurements made with two electrode valves. It is, unfortunately, rare in accounts of experiments on critical potentials to find the currents given in anything except arbitrary units, so that it is impossible to say to what extent the energies of the electrons were affected by the force due to the space-charges ; but as hot filaments are generally used as the source of electrons, it may be concluded that the emission currents were certainly more than a few microamperes and were therefore large enough to cause considerable changes in the field of force.

The gas-free space considered is, of course, the most favourable for lack of distortion by space-charge. If gas is present the electrons move with less velocity and the space-charge effect is considerably increased and is much greater than that indicated by the preceding calculations.

The general conclusion to be drawn therefore from these calculations is that the velocities of the electrons traversing force free spaces are generally less than the velocities with which they are projected through the first grid.

I am indebted to Prof. Townsend for advice and criticism.

XIII. *Some Observations on Movements of Particles in Kundt's Tube.* *By* C. O. Pringle, *B.Sc., Dept. of Physics, Queen's University, Belfast* *.

[Plate I.]

DURING an attempt to reproduce the results obtained by Andrade and Lewer † with an electrically-operated Kundt's tube, some phenomena have been observed to which attention does not yet appear to have been drawn.

The note used, of frequency about 900 per second, was generated by a valve oscillator and amplified by a power

* Communicated by Prof. W. B. Morton, M.A.

† Andrade and Lewer, 'Nature,' cxxiv. p. 724 (1929).

valve followed by a 2-valve " push-pull " amplifier before being applied to the tube through a loud-speaker unit, the cone of which was replaced by a cork disk which just fitted into the end of the tube without touching the glass. The current through the unit was measured by a thermo-couple, and had a maximum of about 20 milliamps. When the tube was working on maximum power the effect produced was not quite so strong as that which can be obtained with a Kundt's tube of the ordinary type when the vibrating rod is stroked vigorously.

Silica and cork-dust have been found to give best results. The silica was prepared in the laboratory by the action of sulphuric acid on powdered glass and fluorspar *, and was not so fine as the commercial product. The latter, however, did not give satisfactorily any of the results obtained.

Using cork-dust in a glass tube $\frac{3}{4}$ in. in diameter, a number of disks were obtained at an antinode. Of these, the central one was similar to that photographed by Andrade and Lewer. The others were less dense, those nearer the antinode being more like the central one, those further away becoming merely partial rings round the upper part of the inside of the tube. These disks and rings, when first formed, have a a spacing approximately the same as that of the secondary striæ in the bottom of the tube; they do not remain stationary, however, but tend to close in and merge into each other or into the central disk.

With comparatively large quantities of silica in the tube some of the antinodal ripples may extend to the top of the tube, forming " solid " disks of almost stationary particles. Several of these disks are formed at first, but all but one or two break down in a few seconds as the dust is carried to the nodes. There is a continual fall of particles from each side of a disk into the bottom of the tube, and in the disk a corresponding rise of particles from the bottom of the tube. Plate I., *a*, shows two of these disks and the antinodal ripples on each side. These disks are possibly of the type obtained by Cook †. They can be obtained easily by a method corresponding to his, namely, by inserting a smaller tube, of diameter $\frac{1}{2}$ in., containing silica into the end of a 1-in. diameter Kundt's tube, as shown at *b* in

* " Silicón," Thorpe's Dict. App. Science, vi. p. 84 (1926).
† Cook, ' Nature,' cxviii. p. 157 (1926).

Plate I. Another print (Plate I., *c*) from the same photograph shows more clearly the disks at the two antinodes. A closer view of the disks in this tube is given in Plate I., *d*. In this photograph three disks are shown, and between the second and third from the right-hand side is another disk in the act of breaking down.

The disks in the small tube are steadier and more permanent than those in the larger tube, especially when the end of the tube is tightly closed.

If a sliding stop is used there is a gradual movement of the disks towards that end of the tube. This is accompanied by a breakdown of each disk as it approaches the node and the formation of new disks at the antinodes, so long as there is enough silica present.

Cork-dust in this secondary tube gives the light disks and rings of the type mentioned above at each antinode, but in a smaller tube, of diameter $\frac{3}{8}$ in., cork-dust gives the "solid" disks.

In addition to the streaks * due to particles vibrating in a line parallel to the axis of the tube, which in the apparatus used were mainly microscopic, streaks are obtained from particles vibrating in a plane perpendicular to the length of the tube, and such streaks are found in all directions in this plane. They are found when very small quantities of cork-dust or silica are present, and are of different lengths up to about 5 mm. The particles from which they arise have not all the same frequency of oscillation; some have a frequency which may be that of the note supplied, others have a much lower frequency, and in some cases their motion can easily be followed by the eye. Occasionally these short bright lines remain steady for a few seconds, but more often they move up and down, or along the tube near the walls, or shoot from side to side across the tube until they collide with another particle. In Plate I., *e*, some stationary streaks of this type are indicated by arrows. This photograph was taken from slightly above the tube, and the particles forming partial striæ in the bottom of the tube therefore appear as if a short distance up the wall of the tube.

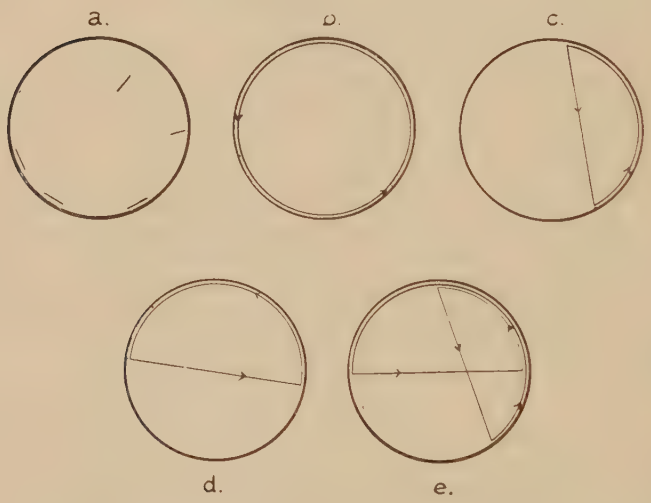
Fig. 1*a* is a diagram of the cross-section of the tube showing some of the positions which may be taken up by the streaks.

* Andrade and Lewer, *loc. cit.*; Carrière, *Journal de Physique*, x. p. 198 (1929).

The microscope reveals some particles which have simultaneously both this type of vibration at low frequency and a vibration parallel to the axis at a much greater frequency. These appear as small rectangles of light.

A particle may also move in a small circular orbit giving a ring of light, or two such particles may have intersecting orbits giving intersecting rings. These two particles do not collide until disturbed by the approach of another particle. These circular paths are only visible in a microscope, but can be found easily near the end of an

Fig. 1.



Cross-sections of tube, with paths of particles.

antinodal ripple or near a larger particle in the bottom of the tube; they only exist when there is a very small quantity of dust in the tube.

With small quantities of dust in the tube, particles have been observed moving round the inside of the tube in circles, the planes of which are perpendicular to the axis of the tube. Such an orbit is shown diagramatically in fig. 1 *b*. If there are so few particles that collisions are rare, a single particle may make a large number of complete circuits of the tube at a rate of about 2 per second. The particles appear to be thrown up from the bottom of

the tube, from between ripples if there is enough dust present to form ripples. Two particles may travel round the tube in opposite directions in orbits just far enough apart to prevent collisions. If two such particles meet they either move off along the wall of the tube or fall into the bottom, where they may again take up the above motion. When very few particles are present some have been observed to move with a longitudinal drift imposed on the above motion, giving a spiral the pitch of which is the same as the spacing of the ripples. With larger quantities of dust the particles start up the walls and collide with other particles, and it is suggested that it is such particles which form the disks obtained by Andrade and Lewer.

Particles have also been observed tracing an orbit which lies in a plane perpendicular to the axis of the tube, and which consists not of a complete circle, but of an arc and chord. The chord may be of any length up to a diameter of the tube, and may have any inclination to the horizontal. A particle may trace out this orbit a large number of times before being displaced. This type of orbit is indicated in figs. 1 *c* and 1 *d*, and it may also be traversed by a particle which is itself in oscillation in the plane perpendicular to the axis of the tube, as described above. A particle may also change from one orbit to another and back to the first, giving the more complex path (fig. 1 *e*). Observations were made in which such a path was traced out up to six times.

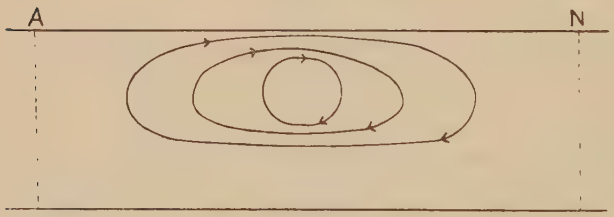
When a quantity of cork-dust is placed at the antinode nearest to the sounding-disk in the tube, and the stop is so far along the tube that there are several antinodes, some very fine dust is carried to the second antinode. This dust moves in a manner which indicates the presence of a current of air from antinode to node near the walls of the tube, and from node to antinode in the centre of the tube. The existence of this current was proved on theoretical grounds by Lord Rayleigh *.

The particles can be observed moving up the centre of the tube towards the antinode, and some can be seen rising into the upper part of the tube, where they move back again near the wall, falling as they approach the node and retracing the path. Fig. 2 is a diagram showing the

* Rayleigh, Phil. Trans. clxxv. part 1, p. 1 (1884).

general position of these paths. This motion has also been observed with single particles of silica when there are only a few particles in the tube. The orbit never has a length equal to the full distance from antinode to node, but varies in length from about two-thirds of this distance down to a size where it is almost circular and situated half way between antinode and node. A single particle has been observed to make up to four or five complete circuits of this type, each being of about one second in duration, before it was disturbed by collision with another particle. In the

Fig. 2.



Orbital motion of particles, indicating presence of air-currents.

lower half of the tube in this case the tendency of the particles to form ripples and the greater concentration of particles appear to prevent the formation of such orbits.

The writer is greatly indebted to Mr. J. Wylie, B.A., who suggested this work, and has given valuable assistance during its progress. He also desires to thank other members of the staff of the Department for their help at various times.

Key to Plate.

a. Two solid disks with antinodal ripples in a $\frac{3}{4}$-in. diameter tube.
b. A secondary tube, $\frac{3}{8}$ in. in diameter, inserted into the end of a 1-in. diameter Kundt's tube giving disks at two antinodes.
c. The antinodal disks shown more clearly than in *b*: same photograph as *b*.
d. The disks in the secondary tube, viewed obliquely.
e. Short streaks of light due to strongly illuminated vibrating particles: only the one against the middle arrow shows clearly in the reproduction. (Magnification, $\times 1{\cdot}05$).

XIV. *On the Behaviour of Electrons amongst the Molecules NH_3, H_2O, and HCl.* *By* V. A. Bailey, *M.A., D.Phil. (Oxon), F.Inst.P., Associate Professor of Physics, University of Sydney, and* W. E. Duncanson, *B.Sc., Science Research Scholar, University of Sydney* *.

1. THE easy familiarity with which some chemists and physicists discuss the electrical properties of molecules when considering chemical combination or the motion of electricity in gases is apt to be misleading, as there are several of these properties about which little is known.

For molecules which have a negligible power of combining with electrons, the most successful and unimpeachable methods of investigation are those used by J. S. Townsend and his collaborators; but with molecules like NH_3 and HCl, which can capture electrons comparatively frequently, there have not been, until recently †, any methods for determining their behaviour towards slow electrons which are at all comparable with the former in reliability and the wealth ‡ of information which can be derived from them.

In this communication we describe how these recent methods may be used to determine the four quantities u, L, λ, h for electrons moving in the gases NH_3, H_2O, and HCl under the action of uniform electric fields, where

u is the velocity of agitation of an electron,

L its mean free path at 1 mm. pressure of the gas,

λ its fractional loss of energy at a collision with a molecule, and

h is the probability of its becoming attached at a collision.

* Communicated by the Authors.

† V. A. Bailey, Phil. Mag., July 1923, p. 213; October 1925, p. 825. V. A. Bailey and J. D. McGee, Phil. Mag., December 1928, p. 1073. V. A. Bailey, Phil. Mag., April 1930, pp. 560 and 625.

‡ The methods of Ramsauer and Mayer give information only about the apparent sizes of molecules, and that of Cravath could determine only the coefficients of attachment α.

2. *Description of the Methods.*

These four quantities can be calculated * by means of the following formulæ :—

$$\left.\begin{aligned} u &= 1{\cdot}15\times10^{7}\sqrt{k}\ \text{cm./sec.},\\ \mathrm{L} &= 8\times10^{-9}\mathrm{W}\sqrt{k/(\mathrm{Z}/p)}\ \text{cm.},\\ \lambda &= 1{\cdot}86\times10^{-14}\mathrm{W}^{2}/k,\\ h &= 7\times10^{-16}(\alpha/\mathrm{Z})\mathrm{W}^{2}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

where p is the pressure of the gas, in mm. of mercury,

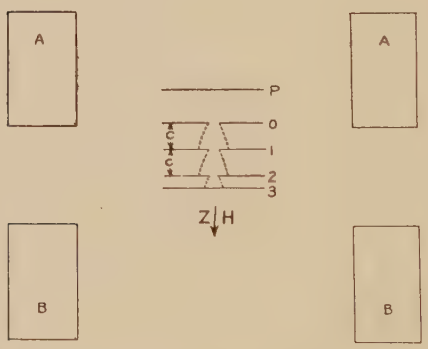
Z the electric intensity, in volts/cm.,

k the mean energy of agitation of an electron in terms of that of a molecule at 15° C.,

α the probability of attachment of an electron in moving unit distance in the direction of Z, and

W is the mean drift velocity of an electron, in cm./sec.

Fig. 1.



The apparatus used to determine k, α, and W is simply represented by fig. 1. Five parallel disks P, 0, 1, 2, 3 are kept at the potentials necessary to produce the uniform field Z throughout the space in which the electrons move, the disks 0, 1, and 2 containing parallel and superposed

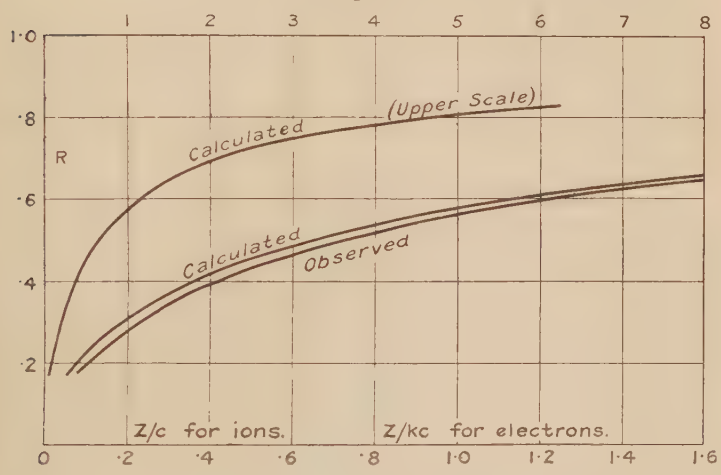
* *Vide* J. S. Townsend, 'Motion of Electrons in Gases' 1925 (O.U. Press), and V. A. Bailey, Phil. Mag., October 1925, p. 843.

slits each 4 mm. wide and respectively 1·5, 6·2, and 7·2 cm. long. The intervals c between these electrodes can be varied between the values 2 and 4 cm.

Electrons are emitted by P under the action of ultra-violet light, and finally reach the electrodes 1, 2, and 3 in relative proportions which depend on the nature and pressure of the gas in the apparatus as well as on the values of Z and c.

The mutual ratios of the currents to these three electrodes are measured, and from these measurements the ratios S_1 and S_2 are determined, where S is the fraction of

Fig. 2.



the stream which passes through the slit of the electrode that it approaches.

If the streams are composed entirely of negative *ions*, then S_1 and S_2 each become equal to a fraction R, which is known in terms of the ratio Z/c and is represented by the curves in fig. 2.

But when the streams contain both electrons and ions this is not so, and the values of S_1 and S_2 are then used to calculate the quantity

$$a = S_1\left(\frac{R-S_2}{R-S_1}\right).$$

Its value a_1 corresponding to a set of values of c, p, and Z, and its value a_n corresponding to a homologous set nc, np,

nZ are determined, and the points with coordinates (x, y) are plotted, where

$$x = n^2 \quad \text{and} \quad y = \log_{10} a_n.$$

The straight line * determined by these points has its slope equal to $\alpha c/2{\cdot}3$, and its intercept on the y-axis equal to $\log_{10} \mathrm{R}(\mathrm{Z}/kc)$, therefore the value of α can be deduced from the slope, and that of k can be deduced from the intercept by using the curves in fig. 2.

To measure W a uniform magnetic field of intensity H and parallel to Z is produced by means of the coils A and B shown in fig. 1, and is adjusted to a value H_0 at which S_2 becomes equal to R. The velocity of drift may then be calculated by means of the formula †,

$$\mathrm{W} = \frac{\mathrm{Z}}{\mathrm{H}_0}\sqrt{k-1} \times 10^8, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

since k is now known.

3. *Use with* NH_3.

This gas was generated by heating a mixture of pure $\mathrm{NH_4Cl}$ and CaO to about 190° C. in an evacuated flask, dried by means of KOH, twice fractionally distilled from the solid form in liquid-air traps, and finally stored in flasks containing small quantities of $\mathrm{P_2O_5}$.

The observed values of $(\log_{10} a + 1)$ and of H_0 (in gauss) corresponding to various sets of values of c, p, and Z are shown in Table I., each being the mean of at least two observations. Since k, α/p, and W are functions of the ratio Z/p alone, the observations are arranged in groups each of which corresponds to a given value of Z p.

The values of α/p deduced from these numbers, and given in the eighth column, are in excellent agreement with the values found in an earlier ‡ investigation of $\mathrm{NH_3}$.

The numbers deduced for k with the help of the calculated § distribution curve in fig. 2 are also in good agreement with those previously ‖ obtained, but the values of k shown in the ninth column are those determined by means

* V. A. Bailey and J. D. McGee, *loc. cit.* p. 1077.
† V. A. Bailey, Phil. Mag., April 1930, p. 566.
‡ V. A. Bailey and J. D. McGee, *loc. cit.* fig. 9.
§ Obtained by means of a simple calculation which neglects the effect of diffusion to the edges of the slits.
‖ V. A. Bailey and J. D. McGee, *loc. cit.* fig. 8.

of the more reliable distribution curve obtained from observations † on pure hydrogen.

TABLE I.

NH_3.

Z/*p*.	*c*.	*p*.	Z.	$\log_{10}\alpha + 1$.	H_0.	H_0/Z.	α/p.	*k*.	$W \times 10^{-5}$.
4.....	3	1·5	6	·740	604	101	—	1·50*	6·9
6.....	2	1·33	8	—	510	64			
	3	2·00	12	·785	720	60	—	1·55*	12·4
8.....	2	·50	4	—	(255)	(64)			
	2	1·00	8	·732	476	59			
	3	1·50	12	—	708	59	·006	4·3	31
	4	2·00	16	·715	915	57			
10.....	2	·60	6	—	(450)	(75)			
	2	·80	8	—	560	70	—	—	49
	3	1·20	12	—	825	69			
12.....	2	·33	4	·173	340	85	·06		
	4	·67	8	·121	670	84			
	2	·67	8	·326	640	80	·04	30	65
	4	1·33	16	·255	—	—			
16.....	2	·25	4	·104	368	92	·13		
	4	·50	8	·021	755	94			
	2	·50	8	·190	726	91	·12	50	76
	4	1·00	16	·033	—	—			
24.....	2	·17	4	·107	354	88	·21		
	4	·33	8	·017	708	89			
	2	·33	8	·163	702	88	·20	56	84
	4	·67	16	(– ·007)	—	—			
32.....	4	·37	12	—	990	82			
	2	·25	8	·176	650	81	·20	57	92
	4	·50	16	·046	—	—			

* These values of *k* are obtained from the values of S_1 as if no ions were present.

It may be seen from Table I. that the values of α/p obtained with the values 2 and 4 of Z/*c* are in good agreement, a test of the method which was also satisfied in the former work on NH_3, where the two values of Z/*c* were 4 and 8.

The quantities *k* and α/p are represented as functions of Z/*p* by curves in figs. 3 and 4 respectively.

† See for example V. A. Bailey, Phil. Mag., October 1925, p. 835.

In order to provide a test of the method for obtaining W, the values of the ratio H_0/Z are given in the seventh column of the table, as the formula (2) shows that this ratio must remain constant for a given value of Z/p. The numbers show that this rule is closely followed.

Another useful test consists in determining the values of S_1 with the magnetic field H_0 applied and comparing them with the corresponding values of S_2 as in Table II.

Fig. 3.

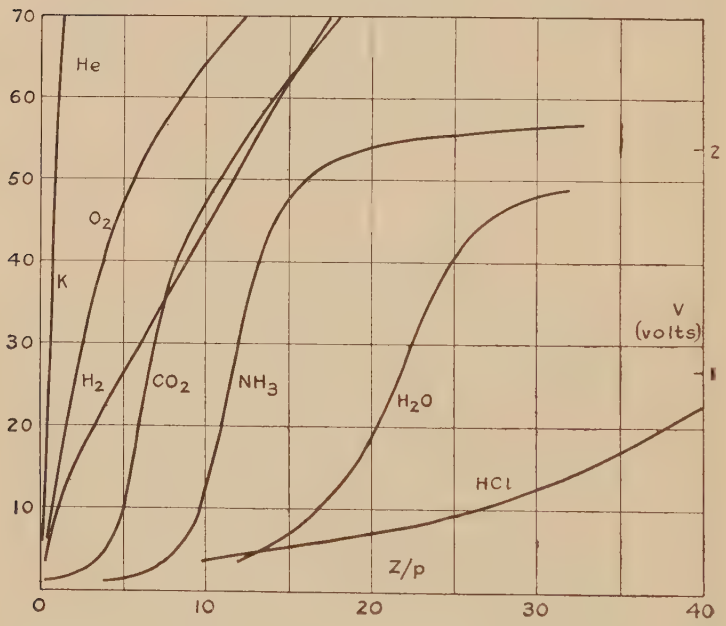
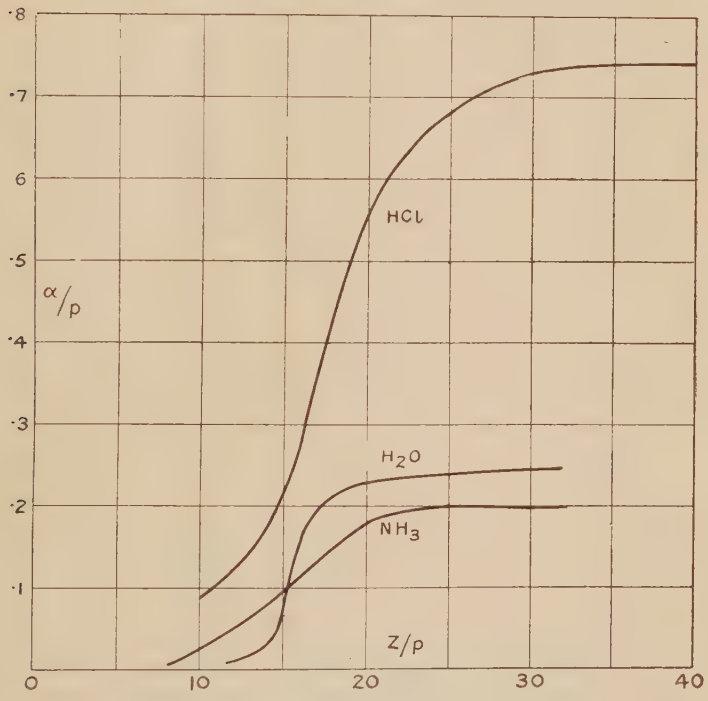


TABLE II.

Z/p.	c.	p.	Z.	H_0.	S_1.	S_2.	R.
8	3	1·5	12	—	·531	·541	
,,	,,	,,	,,	708	·770	·780	·780
16	4	·5	8	—	·180	·392	
,,	,,	,,	,,	755	·692	·690	·690
24	2	·333	8	—	·207	·379	
,,	,,	,,	,,	702	·773	·780	·780

In each instance the theoretical relation $S_1=S_2=R$ is well satisfied, despite the large difference between S_1 and S_2, which exists in the absence of a magnetic field with the higher values of Z/p. For example, with $c=4$ cm., $p=$ ·5 mm., $Z=8$ volts/cm. the values of S_1 and S_2 were ·180 and ·392 respectively; the magnetic field necessary to increase the value of S_2 to that of R (namely ·690) was found to have the value 755 gauss; in the presence of this field the value of S_1 was then observed to be ·692.

Fig. 4.

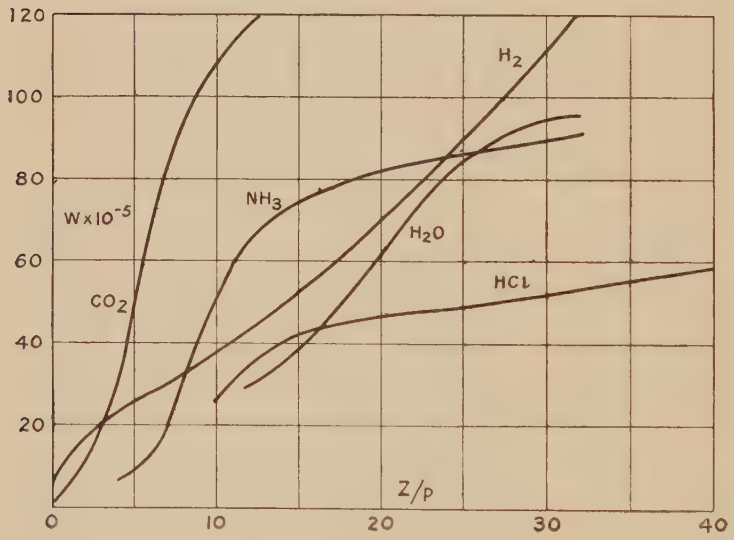


This test in general would only be satisfied if the electrons attained a steady state before passing through the first slit, and if no notable number of positive ions were generated by collisions between electrons and molecules.

The values of W calculated by means of (2) are given in the last column of Table I., and are also represented by a curve in fig. 5.

A few observations of W were also made by means of Townsend's method, in which the stream is deflected through a known angle by means of a transverse magnetic field. With the ratio Z/p equal to 4 and 6 the values of W so determined were independent of the pressure and in agreement with those given in Table I. This is to be expected if permanent ions are absent. For the values 8 and 16 of Z/p the numbers for W were notably lower than those in Table I., which is consistent with the conclusion that the streams contain a large proportion of ions under these conditions.

Fig. 5.



The values of u, L, λ, and h for NH_3, deduced from these results by means of the formulæ (1), are given in Table V. together with V, the energy of an electron expressed in volts. For the purpose of comparison with other molecules the quantities L, λ, and h are expressed as functions of u by curves in figs. 6, 7, and 8 respectively.

4. *Use with* H_2O.

The gas was evaporated from distilled water in an evacuated glass bulb, its pressure being determined by means of a manometer filled with paraffin oil. This

Fig. 6.

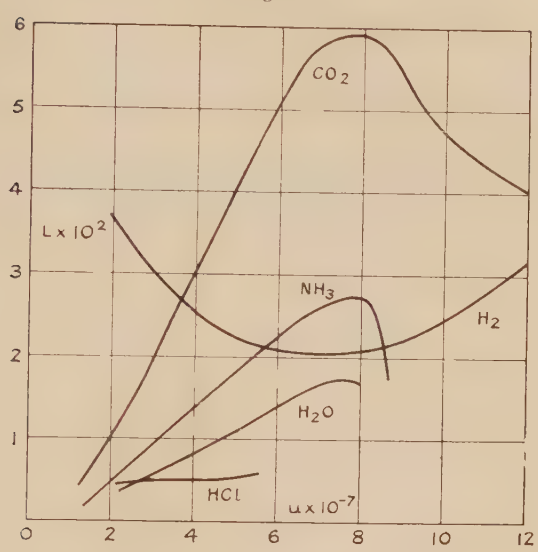
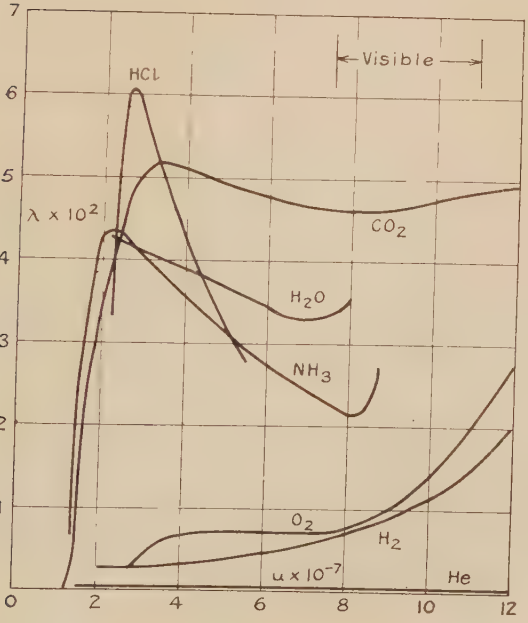

6
5
4
3
2
1
0
2
4
6
8
10
12
CO_2
L x 10^2
NH_3
H_2
H_2O
HCl
u x 10^{-7}

Fig. 7.

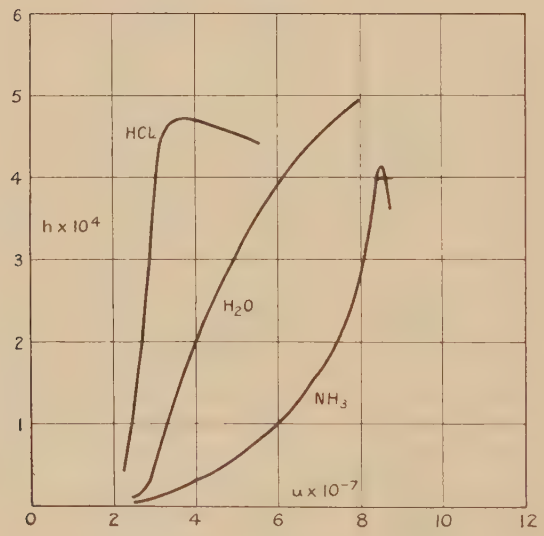

7
6
5
4
3
2
1
0
2
4
6
8
10
12
Visible
HCl
λ x 10^2
CO_2
H_2O
NH_3
O_2
H_2
u x 10^{-7}
He

manometer was standardized by means of hydrogen at a pressure which could be measured with a mercury manometer.

The experimental results are set out in Table III. (which is similar to Table I.), the value of Z/c being 4 throughout.

For values of Z/p near 15 the conditions are somewhat critical, on account probably of the extremely rapid increase of α/p with Z/p. Hence the values of α/p, k, and

Fig. 8.



W for Z/p equal to 14 and 15 are not as accurate as those for the other values given. A more precise exploration of this region would require some improvements in the apparatus used which it has not yet become convenient to make.

The numbers under H_0/Z show that this ratio remains constant for a given value of Z/p as required by the theory.

The values of u, L, λ, and h are given in the second part of Table V., and the curves representing k, α/p, W, L, λ, and h are shown in figs. 3 to 8.

TABLE III.

H_2O.

Z/p.	c.	p.	Z.	$\log_{10}\alpha + 1$	H_0.	H_0/Z.	α/p.	k.	$W \times 10^{-5}$.
12.....	2	·67	8	·769	453	57	·015	3·2	27
	3	1·00	12	·757	668	56			
	4	1·33	16	·742	905	57			
14.....	2	·57	8	·643	429	54	·022	6·8	44
	3	·86	12	—	661	55			
	4	1·14	16	·620	—	—			
15.....	2	·53	8	·623	476	60	·07	7·0	41
	3	·80	12	—	731	61			
	4	1·07	16	·527	—	—			
16.....	2	·50	8	·586	507	63	·17	7·2	39
	3	·75	12	·456	789	66			
	4	1·00	16	·358	—	—			
20.....	2	·40	8	·402	557	70	·23	17	56
	3	·60	12	—	870	72			
	4	·80	16	·154	—	—			
24.....	2	·33	8	·218	580	72	·23	40	84
	3	·50	12	·149	905	75			
	4	·67	16	·015	—	—			
32.....	2	·25	8	·192	569	71	·25	49	96
	3	·38	12	·130	882	73			
	4	·50	16	·029	—	—			

5. *Use with HCl.*

This gas was prepared by removing the air from a glass bulb containing a normally-boiling solution of HCl, roughly drying the evaporated gas over strong sulphuric acid, and fractionally distilling it by means of several liquid-air traps, the first of which contained a small quantity of sulphuric acid. The purified gas was then stored in a glass reservoir which also contained a little sulphuric acid.

The experimental results are set out in Table IV. which is similar to Tables I. and III.. but with Z/c equal to 2.

The values of k and α/p are in fair agreement with those obtained previously * by means of a different instrument and a different method.

* V. A. Bailey and A. J. Higgs, Phil. Mag., Feb. 1929, p. 281.

But it was more difficult to determine H_0 accurately with this gas than with NH_3 and H_2O, on account of the large proportion of ions in the streams and the low values of k and Z. At the higher pressures the intensity of the ultra-violet light appreciably affected the observed values of H_0, which may be due to the effect of self-repulsion of the ions on the divergence of the stream ; consequently the intensity of the light was kept as small as possible.

It can be seen from the numbers in the seventh column of Table IV. that the ratio H_0/Z is not as constant for a

TABLE IV.

HCl:

Z/p.	c.	p.	Z.	$\log_{10}\frac{a}{+1}$	H_0.	H_0/Z.	α/p.	k.	$W\times10^{-5}$.
10.....	2	·40	4	·617	248	62	·09	3·4	25
	3	·60	6	·603	—	—			
	4	·80	8	·533	—	—			
15.....	2	·27	4	·504	201	50	·22	5·9	44
	4	·53	8	·356	457	57			
20.....	2	·20	4	·438	213	53	56	6·6	45
	4	·40	8	·144	522	65			
30.....	2	·13	4	·310	267	67	·73	12	50
	4	·27	8	·056	—	—			
40.....	2	·10	4	·200	310	78	·74	22	60
	4	·20	8	·007	830	104			

given value of Z/p as it is with the other two gases, but it is probable that the numbers corresponding to the lower pressures are correct within about 20 per cent. Should the necessity arise it would be possible to attain greater accuracy.

The values of u, L, λ, and h are given in the last part of Table V., and the curves representing k, α/p, W, L, λ, and h are shown in figs. 3 to 8.

6. *Discussion of Results.*

The results for several other gases are also shown in these figures, as it is of interest to consider the values of some of the above quantities for the different molecules

and to indicate properties of molecules which may be related to the variations of these quantities with the energy of the electrons.

The curves for k (as in fig. 3) are of three types, the first corresponding to the gases* He, Ne, A, the second to H_2, N_2, O_2, NO, CO, and the third to CO_2, NH_3, H_2O, HCl, N_2O, C_2H_4, C_5H_{12}. These groups of molecules are in

TABLE V.

Z/p.	V volts.	$u\times10^{-7}$ cm./sec.	$L\times100$ cm.	$\lambda\times100$.	$k\times10^{1}$.
		NH_3.			
4.....	·055	1·40	·17	·62	—
6.....	·06	1·43	·21	1·83	—
8.....	·17	2·49	·67	4·27	·03
10.....	·45	4·02	1·37	3·54	·32
12.....	1·11	6·29	2·38	2·61	1·2
16.....	1·85	8·12	2·70	2·15	3·1
24.....	2·05	8·57	2·09	2·34	4·1
32.....	2·11	8·67	1·73	2·73	3·7
		H_2O.			
12.....	·14	2·21	·37	4·23	·06
14.....	·21	2·72	·48	4·18	·19
16.....	·32	3·37	·63	4·00	1·3
20.....	·70	4·98	1·07	3·69	3·0
24.....	1·37	7·00	1·65	3·28	4·5
32.....	1·81	8·04	1·69	3·52	5·0
		HCl.			
10.....	·14	2·24	·41	3·3	·4
15.....	·20	2·64	·51	6·0	1·7
20.....	·26	3·04	·49	5·6	4·1
30.....	·45	4·02	·49	4·2	4·7
40.....	·83	5·46	·56	2·8	4·4

order of increasing complexity, and also behave differently in regard to the absorption of light. The first group is extemely transparent to light of all wave-lengths down to the lower limit of the ultra-violet region; the second

* J. S. Townsend, *loc. cit.* M. F. Skinker and J. V. White, Phil. Mag., Oct. 1923, p. 630. H. L. Brose, Phil. Mag., Sept. 1925, p. 536. J. Bannon and H. L. Brose, Phil. Mag., Nov. 1928, p. 817. J. D. McGee and J. C. Jæger, Phil. Mag., Dec. 1928, p. 1107.

(excepting CO) absorbs light notably only in the ultra-violet region; and the third is known * to have strong absorption-bands in the infra-red region.

Similar remarks may be made about the curves for the fraction λ (as in fig. 7); but a more interesting fact about them is the correspondence between the magnitudes of λ for any gas and its light-absorption. If the light-frequency ν is given in terms of the electronic energy by Einstein's relation $h\nu = \frac{1}{2}mu^2$, then the larger values of λ correspond to values of ν in the neighbourhood of strong absorption-bands, and the smaller values of λ correspond to regions of small light-absorption †.

The larger values of λ are of the order of 6 per cent., which is roughly the same as the average order of the fractional change of frequency in the Raman effect. A closer examination of the relation between λ and the absorption and scattering of light requires much more complete information about the light-intensities involved than is now available.

The curves for the mean free path L (in fig. 6) have similar forms for the molecules CO_2,, NH_3, and H_2O. With each of these L increases to a maximum value as the velocity u increases, and a similar but smaller change occurs for HCl. It is interesting to notice that the largest value of L obtained by these methods, namely 16 mm. in argon, is 800 times as large as the smallest value, namely ·02 mm. in NH_3.

The curves for α/p (in fig. 4) also show a mutual resemblance for the gases NH_3, H_2O, and HCl, each increasing with Z/p from a low to a maximum value. The experiments of Skinker ‡ and White appear to indicate that N_2O behaves similarly. But for air, O_2, and NO the experiments show a diminution of α/p with increasing Z/p.

The curves for the probability of attachment h (in fig. 8) all show large increases § of h with the velocity u of an electron which collides with one of the molecules NH_3, H_2O, and HCl. On comparing this with the curves for the mean free path L (in fig. 6), it is seen that in colliding with one of these molecules an electron is more liable

* No absorption data have been found for the gas C_5H_{12}.

† Thus the blueness of the sky and the redness of the setting sun correspond to the decrease of λ for air from ·05 to ·003 over the visible spectrum from short to long waves.

‡ M. F. Skinker and J. V. White, *loc. cit.*

§ *E. g.* for NH_3 the increase is at least a hundredfold.

to remain attached the further it penetrates into the molecule. The same rule applies to the "molecule" of air, and to O_2, NO, and N_2O as far as can be judged from the available evidence.

On the other hand, for the four molecules air, NH_3, H_2O, and HCl the probability of an electron of a given energy becoming attached increases with the apparent size of the molecule.

The rapid diminution of h with u for NH_3, H_2O, and HCl suggests the possibility that, at still lower velocities than those shown, h may be so small that the streams of negative electricity will be composed almost entirely of free electrons. As mentioned in Section 3, this possibility has been verified * for NH_3, but no opportunity has yet occurred to examine it for H_2O and HCl.

It is probable that the properties investigated here are also related to chemical properties of the molecule (*e.g.*, the heat of formation), but no reliable conclusions are possible until a much larger number of kinds of molecules has been studied.

Recently A. Cravath † has published an account of a method for measuring α/p which makes use of an ingenious device (also independently conceived by Van der Graaf) for collecting most of the electrons in a mixed stream of negative particles. He has not yet suceeded in obtaining consistent results with it, but it appears to promise success when suitably modified.

7. *Summary.*

The problem of determining the statistical behaviour of electrons amongst molecules, to which they may become attached, has now been solved for those conditions where ionization by collision is absent and where the negative ions are permanent. The methods used and their application to the gases NH_3, H_2O, and HCl are described in some detail, and are found to give consistent results for the energy of agitation of electrons, their velocity of drift, and their probability of attachment to molecules per unit distance of drift.

* It should be mentioned that Wahlin has also found few ions accompanying a stream of electrons through NH_3 with low values of Z/p.

† A. Cravath, Phys. Rev., April 1929.

From these quantities have been deduced the values of the mean free path L of an electron in each gas, the fraction λ of its own energy which is lost and the probability h of its becoming attached when it collides with a molecule.

The results obtained from these and other experiments appear to show that λ bears some relation to the light-absorbing power of the molecule, and that the probability h for a given kind of molecule varies considerably with the energy of the electron, generally increasing with its penetration into the molecule.

In conclusion we wish to acknowledge our indebtedness to Mr. J. D. McGee for his valuable assistance in the designing and standardizing of the coils used for producing the magnetic fields.

XV. *Contribution to the Kinetic Theory of Vaporization.*—III. *The Vapour Pressure of Solutions.* *By* Samuel Clement Bradford, *D.Sc., The Science Museum, London, S.W.* 7 *.

IN previous papers † Maxwell's theory of the distribution of molecular velocities, which regarded molecules merely as hard, perfectly elastic spheres, has been amplified to take into account the effects of molecular attraction. An expression was thus obtained for the vapour pressure of a pure liquid in terms of molecular attraction, volume, and motion only, and the vapour pressures calculated from this formula agreed remarkably with the observed values for every liquid examined. In the second paper it was suggested that the theory should be capable of extension to the case of solutions of salts in water. This has now been done, and, in spite of the more complicated conditions, the theory gives results almost equally as good for solutions as for pure liquids. This remarkable agreement is evidence that the so-called failure of the classical dynamics is due not to any inherent defect in the method, but to the omission on the part of mathematicians to allow for the mutual attractions of moving particles in close proximity to one another.

* Communicated by the Author.

† Phil. Mag. xlviii. p. 936 (1924); l. p. 1147 (1925).

(i.) *The Vapour Pressure of a Pure Liquid.*

Let us consider a pure liquid in contact with its vapour only, and maintained at constant temperature in a thermostat under ordinary laboratory conditions, so that any heat abstracted from the liquid by the escaping vapour will be supplied immediately by the enclosure, while any heat gained by the vapour will be given up to the surroundings.

Although the molecules of the liquid are not spherical in shape, they will be in continuous motion, and their rapid rotational velocity will maintain a clear spherical space around the centre of rotation of each molecule. As the molecules are electrically neutral, they will repel in some orientations and attract in others; but, as the duration of the attractive encounters is greater, the effect of the attractions will preponderate over that of the repulsions.

Let δ be the mean of the nearest distances of approach of the centres of two molecules during a considerable number of encounters. If we consider a space element dv at a definite position relative to a given molecule, the molecules with their centres within dv will be continually changing their position and attractive forces. During a sufficient interval of time, any point within dv will have been occupied by a molecular centre as often as any other point, and the average force at that point will be the same as at any other point. In measuring the vapour pressure of liquids we are concerned not with instantaneous values, but with average values, during a considerable interval of time. It seems legitimate, therefore, to consider the average values of the molecular forces within a given space element. The space element dv may be situated at any distance from an attracted molecule equal to, or greater than, δ.

The average value of the attraction* between two molecules whose centres are at a distance r has been shown to be approximately

$$f=\frac{c}{r^8}, \quad \ldots\ldots\ldots \quad \text{(i)}$$

where

$$c=\frac{6K\delta^4}{\pi n^2}, \quad \ldots\ldots\ldots \quad \text{(ii)}$$

* Edser, "Molecular Attraction and the Physical Properties of Liquids," Brit. Assoc. 4th Report on Colloid Chemistry, p. 40 (1922).

n being the number of molecules per unit volume and K the cohesion of the liquid as determined by Edser's equation

$$K = \frac{4S}{\delta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

in which S is the surface tension of the liquid.

To find the attraction of the liquid on an escaping molecule, let P be the centre of a molecule at a distance x below the surface AB of the liquid, where $x > \delta$. The attraction of the liquid on P may be taken as equal and opposite to the attraction that would be exerted by a continuous mass of liquid above AB. Molecules in this supposed mass of liquid, whose centres would be between two planes parallel to AB, at distances ξ and $\xi + d\xi$ above AB, would exert on P a resultant attraction equal to

$$\frac{2\pi cn\, d\xi}{(x+\xi)^6} \int_0^{\pi} \cos^6 \sin\theta\, d\theta = \frac{2\pi cn\, d\xi}{7(x+\xi)^6}.$$

The attraction per unit area on P by all the molecules whose centres would be above AB would be equal to

$$\frac{2\pi cn}{7} \int_0 \frac{d\xi}{(x+\xi)^6} = \frac{2\pi cn}{35x^5}. \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

When the distance below the surface AB of the escaping molecule becomes less than δ, that part above AB of a sphere, with radius δ described around the molecule, will contain no centres of attracting molecules. The attracting molecules above AB may now be considered to have their centres within the portions above AB of two spheres, with radii r and $r + dr$ described around the molecule at P. The resultant attraction on P by molecules whose centres would be between these spheres is

$$\frac{2\pi cn\, dr}{r^6} \int_0^{\cos^{-1}\left(\frac{x}{r}\right)} \cos\theta \sin\theta\, d\theta = \frac{\pi cn\, dr}{r^6}\left(1 - \frac{x^2}{r^2}\right),$$

and the total attraction per unit area on P by all such molecules would be

$$\pi cn \int_{\delta}^{\infty} \left(\frac{1}{r^6} - \frac{x^2}{r^8}\right) dr = \pi cn \left\{ \frac{1}{5\delta^5} - \frac{x^2}{7\delta^7} \right\}. \quad . \quad \text{(v)}$$

The work done by the molecule at P in escaping to the surface of the liquid is, therefore,

$$\frac{2\pi cn}{35} \int_{-\infty}^{-\delta} \frac{dx}{x^5} + \pi cn \int_{-\delta}^{0} \left(\frac{1}{5\delta^5} - \frac{x^2}{7\delta^7}\right) dx = \frac{\pi cn}{6\delta^4}. \quad \text{(vi)}$$

An equal amount of work must be done by the molecule in escaping completely from the surface to infinity, so that, neglecting the small attraction of the vapour, the total work done by a particle of liquid in passing into the vapour is

$$W = \frac{\pi c n}{3\delta^4} = \frac{2K}{n} \quad \text{(vii)}$$

Giving n its value $\frac{\rho}{M} \times 6{\cdot}23 \times 10^{23}$, ρ being the density of the liquid and M its molecular weight, we have

$$W = 3{\cdot}21 \times 10^{-24} \frac{MK}{\rho} \quad \text{(viii)}$$

The vapour of the liquid is formed by the particles that strike the surface of the liquid with sufficient velocity normal to the surface to accomplish the work W and escape from the liquid.

The number of such particles is determined by Maxwell's law of the distribution of molecular velocities, bearing in mind that the particles in the interior of the liquid are moving under the influence of molecular forces.

The number of particles in unit volume of the liquid that have velocities whose vertical components lie between u and $u + du$ is

$$\frac{n_s}{\sqrt{\pi} V_{ps}} e^{-\frac{u^2}{V_{ps}^2}} . du, \quad \text{(ix)}$$

where n_s is the concentration of the liquid particles and V_{ps} Maxwell's most probable speed of the particles. Therefore the number of particles per unit volume, having velocities normal to the surface between u and $u + du$, that strike the surface from below is

$$\frac{n_s}{V_{ps}\sqrt{\pi}} e^{-\frac{u^2}{V_{ps}^2}} . u\, du. \quad \text{(x)}$$

But of these, only those having velocities normal to the surface equal to, or greater than, a certain critical velocity s will be able to escape from the attraction of the liquid and pass into the vapour. The total number of such particles is

$$\int_s^\infty \frac{n_s}{V_{ps}\sqrt{\pi}} e^{-\frac{u^2}{V_{ps}^2}} . u\, du = \frac{n_s V_{ps}}{2\sqrt{\pi}} . e^{-\frac{s^2}{V_{ps}^2}} \quad \text{(xi)}$$

Now the total number of particles from the vapour that strike the same area of the surface is

$$\int_0^\infty \frac{n^s}{V_{pl}\sqrt{\pi}} e^{-\frac{u^2}{\overline{V_{pl}}^2}} . u\,du = \frac{n_l V_{pl}}{2\sqrt{\pi}}, \quad . \quad . \quad \text{(xii)}$$

where n_l is the concentration of the vapour and V_{pl} Maxwell's constant for the vapour phase.

The greater attraction of the liquid ensures that all particles striking the surface from above return to the liquid. In equilibrium, the number of particles escaping from the liquid must be equal to the number returning, so that from (xi) and (xii)

$$\frac{n_s V_{ps}}{2\sqrt{\pi}} . e^{-\frac{s^2}{\overline{V_{ps}}^2}} = \frac{n_l V_{pl}}{2\sqrt{\pi}}$$

$$\text{or} \qquad n_l = n_s \frac{V_{ps}}{V_{pl}} e^{-\frac{s^2}{\overline{V_{ps}}^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiii)}$$

Previously, in attempting to apply Maxwell's law of the distribution of molecular velocities to systems of attracting particles, the mistake has been made of assuming that the most probable speeds of the particles in such a system will be the same as in a perfect gas at the same temperature. Since, however, the particles attract one another, it follows from the definition of a force that the speeds in a system of attracting particles cannot be the same as in a medium composed of inert particles. That is to say, the law of the equipartition of energy applies only to perfect gases. Therefore V_{ps} is not equal to V_{pl}, and it is necessary to make allowance for the effect of the forces of attraction. Since we may assume that the forces are distributed in magnitude and direction according to the laws of probability, we may write

$$V_{ps} = \lambda V_{pl}, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv)}$$

where λ is a function of the forces of attraction in the medium.

If v_l be the volume occupied by the number N of molecules in a gramme molecule of the given substance in the vapour state, and v_s the volume of the same number of molecules in the liquid condition, then, allowing for the volume occupied by the molecules,

$$n_l = \frac{N}{v_l - b_l} \quad \text{and} \quad n_s = \frac{N}{v_s - b_s},$$

where b_l and b_s are the apparent volumes of the molecules in either state, defined by Kleeman * as the quantities whose magnitudes affect the external pressure at constant temperature and volume, but not the average velocity of translation of the molecules.

Putting

$$v_s - b_s = \Phi_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xv)}$$

and

$$v_l - b_l = \Phi_l, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xvi)}$$

equation (xiii) becomes

$$\Phi_l = \frac{\Phi_s}{\lambda} e^{\frac{s^2}{\lambda^2 V_{pl}^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xvii)}$$

As a first approximation we may take V_{pl}, the most probable speed of the particles in the vapour, as equal to V_p, the most probable speed in a perfect gas, so that

$$V_{pl}^2 = \left(\frac{V}{1{\cdot}23}\right)^2,$$

where V is the average kinetic energy velocity in the gaseous state, and is determined by the equation

$$\tfrac{1}{2} m V^2 = 2{\cdot}012 \times 10^{-16} T,$$

m being the absolute weight of a particle and T the absolute temperature.

Now the critical velocity s fulfils the relation

$$\tfrac{1}{2} m s^2 = W,$$

as given by equation (viii). Making use of these relations, equation (xvii) becomes

$$\Phi_l = \frac{\Phi_s}{\lambda} e^{\frac{7{\cdot}52 \times 10^{15} W}{\lambda^2 T}} \quad . \quad . \quad . \quad . \quad . \quad \text{(xviii)}$$

But the pressure of the vapour in atmospheres is

$$p = 81{\cdot}84 \frac{V_t}{V} \frac{T}{\Phi_l},$$

where V_t is Kleeman's total average velocity of a molecule in the vapour state, and may be taken as approximately equal to V.

* 'A Kinetic Theory of Gases and Liquids,' New York, 1920.

From equations (viii) and (xviii) we have, therefore,

$$p = 81{\cdot}84\frac{T\lambda}{\phi_s}e^{-\frac{2{\cdot}414\times10^{-8}KM}{\lambda^3\rho T}} \quad . \quad . \quad . \quad . \quad (xix)$$

It has been shown that the cohesion K can be calculated with considerable accuracy from Edser's equation (iii), in which δ is given by the formula

$$\delta = \left(\frac{3{\cdot}24M}{2{\cdot}016\rho_m}\right)^{1/3} \times 10^{-8}, \quad . \quad . \quad . \quad . \quad (xx)$$

ρ_m being the density of the liquid near the freezing-point. Writing

$$\delta' = \delta \times 10^8 \quad \text{and} \quad \frac{M}{\rho} = v_s,$$

the pressure of the vapour becomes

$$p = 81{\cdot}84\frac{T\lambda}{\phi_s}e^{-\frac{9{\cdot}665Sv_s}{\lambda^2T\delta'}}.$$

This applies to a non-associated liquid. Should the liquid be associated, its molecular weight would be A . M, where A is the degree of association and M the molecular weight of the unassociated substance, so that the molecular and co-volume of an associated liquid become Av_s and $A\phi_s$ respectively. Similarly, the average molecular diameter becomes $A^{1/3}\delta$. It should be noticed that A is not an arbitrary factor, but represents the actual physical state of the liquid. Therefore the vapour pressure in atmospheres of an associated liquid is

$$p = 81{\cdot}84\frac{T\lambda}{A\phi_s}e^{-\frac{9{\cdot}665Sv_sA^{2/3}}{\lambda^2T\delta'}} \quad . \quad . \quad . \quad (xxi)$$

or

$$p = 81{\cdot}84\frac{T\lambda}{A\phi_s}e^{-\frac{2{\cdot}416K'v_sA^{2/3}}{\lambda^2T}}, \quad . \quad . \quad . \quad (xxii)$$

where $K' = K \times 10^{-8}$.

This formula assumes that for every particle, associated or unassociated, which approaches the surface of a liquid with a velocity normal to the surface equal to, or greater than, the critical velocity s, a single particle is communicated to the vapour. The assumption is not entirely without

justification. But the complete analysis would require a knowledge of the actual values of the attractions of the associated and unassociated particles, and at present these data are lacking. However, when A is small, the expression (xxi) is sufficiently accurate, as Table II. shows. The values of ϕ_s are given approximately by the relation

$$\phi_s = v - \frac{S'^3}{4}. \quad . \quad . \quad . \quad . \quad . \quad \text{(xxiii)}$$

In the equation (xxi) the value of the variable λ remains to be determined. This function, which is the ratio of the most probable speed of the particles in the given liquid to that in a perfect gas, was considered by Kleeman, who calculated its value for CO_2 at 40° and 112 atmospheres pressure to be 1·6. Actually this is near the figure that the present writer has found for water under ordinary conditions.

TABLE I.

Liquid.	t.	$K \times 10^{-8}$.	λ.
n-Hexane	18°	11·47	1·270
Toluene	18°	21·18	1·390
Mercury	200°	599·0	1·915

What is needed, however, is a direct method of deducing λ from the physical condition of the liquid. In previous papers a relation between λ and the density of the liquid was obtained that worked very well for a variety of organic liquids. But for water the relation was not so good, and it seemed desirable to endeavour to trace a direct relation between λ and the cohesion of the liquid.

Three liquids were selected as being unlikely to be much associated. Their cohesions were calculated from Edser's formula (iii), and the values of λ necessary to make the calculated vapour pressures fit the observed figures were determined. The values of K and λ are given in Table I.

Putting

$$\lambda - 1 = y,$$

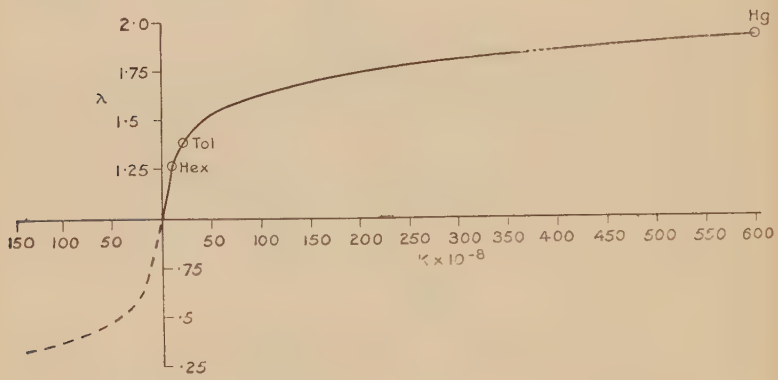
the relation between K and y was assumed to be of the form

$$K = ay + by^3 + cy^5,$$

which gives $\lambda=1$ for $K=0$, the condition corresponding to a perfect gas. The coefficients were determined from the data in Table I., and the equations became

$$K'=42{\cdot}16y-64{\cdot}7y^3+952y^5. \quad . \quad . \quad \text{(xxiv)}$$

The relation between λ and K is expressed graphically in the following curve :—



Either the equation or the curve can be used to find the value of λ from which to calculate the vapour pressure of a pure liquid from the formula (xxi), as has been done in Table II. Although the equation (xxiv) must still be regarded as approximate, the agreement between the observed and calculated values of the vapour pressures shows that the cohesion of the medium has such an effect on the most probable speed of the particles as has been supposed, and that, when this is allowed for, the kinetic theory is sufficient to explain the vapour pressures of liquids.

If the calculated value of the vapour pressure does not agree exactly with the observed value, association is indicated, and a value of A can be determined that will give a figure for the cohesion K, which, together with the corresponding value of λ, leads to the observed value of the vapour pressure. It will be seen that the necessary values of the association agree very well with those calculated by more empirical methods by Ramsay and Shields *. It will be noticed that, in certain cases, the use of equation (xxiv) gives a very slightly lower value of the association factor at lower temperatures for the same liquid.

* J. C. S. lxiii. p. 1089 (1893).

This suggests that in reality the curve should rise a very little more quickly. The effect of this would be to give a rather higher value of λ, say about 1·63 for water, so that the association would work out at about 3·00 with $K = 65·2$. This is, perhaps, a more likely value. The equation (xxiv) may be said to be fairly definite for the region between $\lambda = 1·275$, $K = 11·75 \times 10^8$, and $\lambda = 1·44$, $K = 28·07 \times 10^8$, which covers most of the liquids in the table. Beyond the latter point the curve is only approximate.

These calculations are also of interest in showing that Edser's formula (iii) written in the form

$$K = \frac{4S}{A^{1/3}\delta},$$

with the introduction of an association factor, provides, for the first time, an accurate method of calculating the cohesion of a liquid. Previous methods of estimating this quantity have given values varying between wide limits, such as from 1·710 to 3·570 for toluene, 1·919 to 7·140 for acetic acid, and 3·645 to 17·300 for water. Unless a really accurate method of determining the cohesion of a liquid were available, there could be no hope of calculating its vapour pressure.

(ii.) *The Surface Tension of a Solution.*

Before proceeding to extend equation (xxi) to the case of a solution, it is interesting to develop a formula for the surface tension of a solution. If we neglect, for the time being, the change in concentration in the surface layers, the surface tension of a solution may be determined very simply by Gauss's method.

The surface tension of a liquid is equal to half the work W done per unit area of a surface AB in separating the liquid below AB from that above it.

Let δ_1 and δ_2 be the least distances of approach of the liquid molecules M_1 and solute molecules M_2 respectively, c_1 and c_2 the corresponding coefficients of attraction, and n_1 and n_2 the concentrations of the particles :

(1) The work done in removing to infinity the solution that is at a distance below AB greater than δ.

(1 *a*) Work due to mutual attraction of the solvent molecules M_1.

The attraction exerted by all the solvent molecules M_1

TABLE

Substance.	Molecular weight M.	Temperature °C. t.	Density ρ.	Molecular volume v.	ε'.	Co-volume ϕ.
Acetone	58·05	56	0·710	81·76	4·679	57·14
		20	0·778	73·3		48·68
Aniline	93·04	184	0·867	107·31	5·253	71·07
		54·8	0·990	93·98		57·74
Benzene	78·05	80·5	0·810	96·36	5·192	66·09
		55	0·841	92·8		62·53
Carbon disulphide	76·12	46·8	1·224	62 19	4·618	35·77
Carbon tetrachloride	153·8	76·4	1·489	103·29	5·313	65·80
		25	1·585	97·03		59·54
Chlorobenzene	112·5	131	0·985	126·9	5·417	87·16
		25	1·101	102 18		62·44
Chloroform	119·51	61·2	1·414	84·46	4·994	53·32
		35	1·459	81·91		50·77
Ethyl ether	74·08	34·8	0·698	106·13	5·277	69·39
		25·3	0·707	104·78		68·04
		−20·5	0·758	97·3		60·99
		−75	0·818	90·56		53·82
Ethyl iodide	152·88	72·5	1·830	83·55	5·000	52·30
		20·4	1·934	79·04		47·79
Nitrobenzene	123·06	209	1·031	122 62	5·473	81·63
		100	1·125	109·87		68·88
n-Hexane	86·12	20	0·6595	130·58	5·905	79·10
		25	0·6559	131·30		79·80
Phosphorus trichloride	137·42	77·4	1·471	93·04	5·026	61·30
Pyridine	75·05	114·5	0·882	89 73	4·911	63·12
Toluene	92·06	109·4	0·780	118·13	5·383	79·14
		26	0·860	107·05		68·06
Water	18·02	100	0·958	18·8	3·095	11·50
		18	0·9986	18·045		10·633
Mercury	200·6	200	13·113	15·298	2·88	9·33
		17·5	13·552	14·802		8·83

II.

Surface-tension S.	$K \times 10^{-8}$.	λ.	Association A.		Vapour pressure p.			
					Calculated.		Observed.	
			From vapour pressure.	R. & S.	Atmospheres.	mm.	Atmospheres.	mm.
19·4	15·69	1·332	1·18		1·02		1·00	
23·1	18·09	1·360	1·30	1·26		181		180
24·3	17·51	1·354	1·185	1·05	0·994		1·00	
39·5	28·07	1·440	1·23			4·09		4
20·7	15·49	1·330	1·09	1·01	0·998		1·00	
23·8	17·9	1·358	1·075			332		327
27·3	21·84	1·396	1·27	1·07 at 32°	1·01		1·00	
20·2	15·03	1·324	1·035	1·01 at 46°	0·987		1·00	
25·4	18·96	1·368	1·026			117		116
19·0	14·0	1·312	1·007		0·995		1·00	
32·9	23·9	1·412	1·05	1·03		12		12
21·8	16·64	1·346	1·13		1·04		1·00	
24·8	19·14	1·370	1·12			307		308
15·9	12·03	1·280	1·005	0·99	0·994		1·00	
16·7	12·62	1·291	1·009			536		540
21·5	16·22	1·340	1·015			67		67
28·5	21·1	1·390	1·073			0·9		0·9
22·3	16·88	1·347	1·18	0·96	1·02		1·00	
28·1	21·38	1·392	1·163	1·01 at 46°		109		108
21·2	14·50	1·318	1·22	1·13 at 156°	1·005		1·00	
29	19·27	1·371	1·33	0·93 at 78·4°		21·4		21
17·41	11·75	1·275	1·005			118		120
16·93	11·47	1·270	1·00-			153		153
21·9	17·09	1·350	1·061	1·02 at 32°	1·01		1·00	
25·2	19·88	1·377	1·10	0·93 at 46°	·997		1·00	
19·5	14·47	1·318	1·005		1·01		1·00	
28·4	21·1	1·388	1·00			29·4		29
58·92	54·56	1·540	2·45	2·66	·994		1·00	
72·82	67·75	1·568	2·68	3·68 at 20°		15·7		15·48
431·2	599	1·915	1·00			17·2		17·2
547·2	792	1·970	0·884			0·00106		0·00106

above AB on a molecule of solvent M_1 at a distance x below AB where $x > \delta_1$

$$= \frac{2\pi c_1 n_1}{35 x^5}$$

from (iv).

The work done in removing this molecule to infinity

$$= \frac{2\pi c_1 n_1}{35} \int_x^\infty \frac{dx}{x^5} = \frac{\pi c_1 n_1}{70 x^4}.$$

Describe two planes parallel to AB at distances x and $x + dx$ below AB. Unit area of the layer between these planes will comprise $n_1 dx$ molecules of solvent. The work of removing these molecules to infinity

$$= \frac{\pi c_1 n_1}{70 x^4} n_1 dx.$$

Therefore the work of removing to infinity the whole of the solvent molecules originally at a distance δ_1 or more below AB

$$= W_{1a} = \frac{\pi c_1 n_1^2}{70} \int_{\delta_1}^\infty \frac{dx}{x^4}$$

$$= \frac{\pi c_1 n_1^2}{210 \delta_1^3} \quad \text{(xxv)}$$

(1 *b*) Work due to the attraction of solute molecules M_2 above AB on solvent molecules M_1 below AB.

Describe two planes parallel to AB at distances ξ and $\xi + d\xi$ above AB. Molecules of solute whose centres are between these planes will exert on a solvent molecule M_1 a resultant attraction

$$= \frac{2\pi c_1^{1/2} c_2^{1.2} n_2 d\xi}{(x+\xi)^6} \int_0^{\frac{\pi}{2}} \cos^6 \sin\theta \, d\theta$$

$$= \frac{2\pi c_1^{1/2} c_2^{1/2} n_2 d\xi}{7 (x+\xi)^6}.$$

The attraction exerted on M_1 by all the solute molecules above AB

$$= \frac{2\pi c_1^{1/2} c_2^{1/2} n_2}{7} \int_0^\infty \frac{d\xi}{(x+\xi)^6} = \frac{2\pi c_1^{1/2} c_2^{1/2} n_2}{35 x^5}.$$

The work done in removing this solvent molecule to infinity

$$= \frac{2\pi c_1^{1/2} c_2^{1/2} n_2}{35} \int_0^\infty \frac{dx}{x^5} = \frac{\pi c_1^{1/2} c_2^{1/2} n_2}{70 x^4}.$$

Describe two planes parallel to AB at distances x and $x+dx$ below AB. The number of solvent molecules per unit area between those planes is $n_1 dx$. The work per unit area of AB in removing to infinity the whole of the solvent molecules below AB originally at a distance δ_{12} or more below AB

$$= W_{1b} = \frac{\pi c_1^{1/2} c_2^{1/2} n_1 n_2}{70} \int_{\delta_{12}}^{\infty} \frac{dx}{x^4}$$

$$= \frac{\pi c_1^{1/2} c_2^{1/2} n_1 n_2}{210 \delta_{12}^3}, \quad \ldots \ldots \quad \text{(xxvi)}$$

where δ_{12} is the nearest distance of approach of a solute and solvent particle.

(1 *c*) Similarly the work due to the attraction of solvent molecules M_1 above AB in removing solute molecules M_2 below AB to infinity

$$= W_{1c} = \frac{\pi c_1^{1/2} c_2^{1/2} n_1 n_2}{210 \delta_{12}^3}, \quad \ldots \quad \text{(xxvii)}$$

and

(1 *d*) The work due to the attraction of solute molecules M_2 above AB in removing solute molecules M_2 below AB to infinity

$$= W_{1d} = \frac{\pi c_2 n_2^2}{210 \delta_2^3}. \quad \ldots \ldots \quad \text{(xxviii)}$$

(2) To find the work done per unit area of AB in removing to infinity the solution at a distance x below AB where $x < \delta$.

(2 *a*) Mutual attraction of solvent molecules.

The attraction exerted by all the solvent molecules AB on a solvent molecule at distance $x < \delta$ below AB

$$= \pi c_1 n_1 \left\{ \frac{1}{5 \delta_1^5} - \frac{x^2}{7 \delta_1^7} \right\} \quad \ldots \quad \text{(xxix)}$$

from (v).

The work of removing this molecule to a distance δ_1 from AB

$$= \pi c_1 n_1 \int_x^{\delta_1} \left(\frac{1}{5 \delta_1^5} - \frac{x^2}{7 \delta_1^7} \right) dx$$

$$= \pi c_1 n_1 \left(\frac{\delta_1 - x}{5 \delta_1^5} \quad \frac{\delta_1^3 - x^3}{21 \delta_1^7} \right).$$

The work done per unit area of AB in removing to a distance δ_1 all the solvent molecules originally at distances between 0 and δ_1 below AB

$$= W_{2a} = \pi c_1 {n_1}^2 \int_0^{\delta_1} \left(\frac{\delta_1 - x}{5{\delta_1}^5} - \frac{{\delta_1}^3 - x^3}{21{\delta_1}^7} \right) dx$$

$$= \frac{9\pi c_1 {n_1}^2}{140{\delta_1}^3}. \quad . \quad . \quad .

(2 *c*) Similarly the work due to the attraction of solvent molecules above AB on solute molecules below

$$= W_{2c} = \frac{9\pi {c_1}^{1\cdot 2} {c_2}^{1\cdot 2} n_1 n_2}{140 {\delta_{12}}^3}, \quad . \quad . \quad . \quad \text{(xxxiv)}$$

and

$$W_{3c} = \frac{\pi {c_1}^{1/2} {c_2}^{1/2} n_1 n_2}{70 {\delta_{12}}^3}. \quad . \quad . \quad . \quad . \quad \text{(xxxv)}$$

(2 *d*) Likewise the work due to the attraction of solute molecules above AB on solute molecules below

$$= W_{2d} = \frac{9\pi c_2 {n_2}^2}{140 {\delta_2}^3}, \quad . \quad . \quad . \quad . \quad \text{(xxxvi)}$$

and

$$W_{3d} = \frac{\pi c_2 {n_2}^2}{70 {\delta_2}^3}. \quad . \quad . \quad . \quad . \quad \text{(xxxvii)}$$

The surface tension is half the sum of all these W's. Writing $\delta_{12} = {\delta_1}^{1\cdot 2} {\delta_2}^{1\cdot 2}$ approximately, we get

$$S_{12} = \frac{\pi}{24}\left(\frac{{c_1}^{1/2} n_1}{{\delta_1}^{3\cdot 2}} + \frac{{c_2}^{1/2} n_2}{{\delta_2}^{3\cdot 2}}\right)^2, \quad . \quad . \quad \text{(xxxviii)}$$

or from (ii),

$$S_{12} = \frac{({K_1}^{1/2} {\delta_1}^{1/2} + {K_2}^{1/2} {\delta_2}^{1/2})^2}{4}; \quad . \quad \text{(xxxix)}$$

from which we have, by (iii),

$$K_2 = \frac{4({S_{12}}^{1/2} - {S_1}^{1/2})^2}{\delta_2}. \quad . \quad . \quad . \quad . \quad \text{(xl)}$$

This formula gives a method of determining the cohesion of the solute particles in a solution from the surface tensions of the pure solvent and the solution.

(iii.) *The Vapour Pressure of a Solution.*

From previous work it will be seen that the attraction of the solvent on a particle of solute at a distance x below the surface of the solution would be

$$\pi c_1 n_1 \left\{\frac{1}{5{\delta_1}^5} - \frac{x^2}{7{\delta_1}^7}\right\} + \frac{2\pi c_1 n_1}{35 x^5}. \quad . \quad . \quad . \quad \text{(xli)}$$

To determine the attraction of the solute molecules on an escaping molecule of solvent; let P be the centre of a molecule of solvent at a distance x below the surface AB of the solution, where $x > \delta_{12}$, δ_{12} being the average of the

nearest distances of approach of solvent and solute molecules. The attraction of the solute molecules in the solution is taken as equal and opposite to the attraction that would be exerted by a similar number and distribution of solute molecules above the surface AB.

Molecules of solute in this imaginary mass of solution above AB, whose centres would be between two planes parallel to AB at distances ξ and $\xi+d\xi$ above AB, would exert on P a resultant attraction equal to

$$\frac{2\pi c_1^{1/2}c_2^{1/2}n_2 d\xi}{(x+\xi)^6}\int_0^{\pi}\cos^6\theta\sin\theta\,d\theta=\frac{2\pi c_1^{1/2}c_2^{1/2}n_2 d\xi}{7(x+\xi)^6}.$$

The attraction per unit area on P by all the molecules of of solute whose centres would be above AB would be

$$\frac{2\pi c_1^{1/2}c_2^{1/2}n_2}{7}\int_0^{\infty}\frac{d\xi}{(x+\xi)^6}=\frac{2\pi c_1^{1/2}c_2^{1/2}n_2}{35x^5}. \quad . \quad \text{(xlii)}$$

When the distance below AB of the escaping molecule becomes less than δ_{12}, that part above AB of a sphere with radius δ_{12} described around P will contain no centres of attracting molecules of solute. These may now be considered to have their centres within the portions above AB of two spheres with radii r and $r+dr$ described around P. The resultant attraction on P by all the molecules of solute whose centres would be between these spheres would be

$$\frac{2\pi c_1^{1/2}c_2^{1/2}n_2 dr}{r^6}\int_0^{\cos^{-1}\left(\frac{x}{r}\right)}\cos\theta\,d\theta$$
$$=\frac{\pi c_1^{1/2}c_2^{1/2}n_2 dr}{r^6}\left(1-\frac{x^2}{r^2}\right),$$

and the total attraction on the solvent molecule at P by all the solute molecules whose centres would be above AB would be

$$\pi c_1^{1/2}c_2^{1/2}n_2\int_{\delta_{12}}^{\infty}\left(\frac{1}{r^6}-\frac{x^2}{r^8}\right)dr=\pi c_1^{1/2}c_2^{1/2}n_2\left\{\frac{1}{5\delta_{12}^5}-\frac{x^2}{7\delta_{12}^7}\right\}.$$
$$. \quad . \quad . \quad \text{(xliii)}$$

Therefore the total work done by the solvent molecule at P in escaping to the surface of the solution

$$=\frac{2\pi c_1 n_1}{35}\int_{-\infty}^{-\delta_1}\frac{dx}{x^5}+\frac{2\pi c_1^{1/2}c_2^{1/2}n_2}{35}\int_{-\infty}^{-\delta_{12}}\frac{dx}{x^5}+\pi c_1 n_1$$
$$\times\int_{-\delta_1}^{0}\left(\frac{1}{5\delta_1^5}-\frac{x^2}{7\delta_1^7}\right)dx+\pi c_1^{1/2}c_2^{1/2}n_2$$

$$\times \int_{-\delta_{12}}^{0} \left(\frac{1}{5\delta_{12}^{5}} - \frac{x^2}{7\delta_{12}^{7}} \right) dx = \frac{\pi}{6} \left(\frac{c_1 n_1}{\delta_1^{4}} + \frac{c_1^{1/2} c_2^{1/2} n_2}{\delta_{12}^{4}} \right). \quad . \quad . \quad . \quad \text{(xliv)}$$

An equal amount of work must be done by the solvent molecule in escaping completely from the surface to infinity, so that the total work done by a particle of solvent in passing from the solution into the vapour

$$= W = \frac{\pi}{3} \left(\frac{c_1 n_1}{\delta_1^{4}} + \frac{c_1^{1/2} c_2^{1/2} n^2}{\delta_{12}^{4}} \right). \quad . \quad . \quad . \quad \text{(xlv)}$$

The next step is complicated by the difficulty that although particles of one kind obey Maxwell's law of the distribution of molecular velocities, as modified by the introduction of λ, when there are two kinds of particles of different masses and attractive forces, neither set will obey Maxwell's law exactly. In the first place the different masses of the particles will involve different values of the most probable speed at a given temperature for each set of particles. Secondly, the attraction of the medium on the two sets of particles with different fields of force will be different. This will modify the most probable speeds of each set. And finally, the most probable speeds of either set will be upset by encounters between the two sets of particles.

It may not be impossible to allow for these reactions, but in a preliminary study, in which there are a number of such difficulties, it is permissible to assume that the deviations from Maxwell's law will not be great.

We have, therefore, from (xiii) the number of solvent particles that escape from the solution is

$$n_l = \frac{n_1}{n_1 + n_2} \cdot n_s \frac{V_{ps}}{V_{pl}} \cdot e^{-\frac{s^2}{V_{ps}^2}}, \quad . \quad . \quad . \quad \text{(xlvi)}$$

where n_s is the total number of molecules in unit co-volume of the solution.

As before, if v_l is the volume occupied by the number N of molecules in a gram molecule of solvent in the vapour state, and v_s is the volume of N molecules of solution in the liquid condition,

$$n_l = \frac{N}{v_l - b_l} = \frac{N}{\phi_l},$$

since the effective volume in which the molecules may move is the co-volume, and

$$n_s = \frac{N}{v_s - b_s} = \frac{N}{\phi_s},$$

where ϕ_l is the co-volume of solvent vapour and ϕ_s that of the solution ;

$$\therefore \quad \phi_l = \frac{n_1+n_2}{n_1} \cdot \frac{\phi_s}{\lambda} \cdot e^{\frac{s^2}{\lambda^2 V_{pl}^2}},$$

giving

$$\phi_l = \frac{n_1+n_2}{n_1} \cdot \frac{\phi_s}{\lambda} \cdot e^{\frac{7{\cdot}52\times10^{15}W}{\lambda^2 T}}, \quad . \quad . \quad . \quad . \quad \text{(xlvii)}$$

or from (xlv)

$$\phi_l = \frac{n_1+n_2}{n_1} \cdot \frac{\phi_s}{\lambda} \cdot e^{\frac{7{\cdot}52\times10^{15}\cdot\pi\left(\frac{c_1 n_1}{\delta_1^4}+\frac{c_1^{1/2}c_2^{1/2}n_2}{\delta_{12}^4}\right)}{\lambda^2 T}};$$

and since . . . (xlviii)

$$p = 81{\cdot}84\frac{T}{\phi_l},$$

$$\therefore \quad p = 81{\cdot}84\frac{n_1 T\lambda}{(n_1+n_2)\phi_s}\, e^{-\frac{7{\cdot}882\left(\frac{c_1 n_1}{\delta_1^4}+\frac{c_1^{1/2}c_2^{1/2}n_2}{\delta_{12}^4}\right)\times10^{15}}{\lambda^2 T}}.$$

. . . (xlix)

For purposes of calculation it is convenient to express n_1 and n_2 in terms of grams. Let w_1 and w_2 be the weights of solvent and solute taken respectively, and let ρ_{12} be the density of the solution.

The volume of the solution is

$$\frac{w_1+w_2}{\rho_{12}}.$$

The number of molecules of solvent in w_1 grams of solvent is

$$\frac{w_1}{M_1}\times6{\cdot}23\times10^{23},$$

where M_1 is the molecular weight of the solvent.

Therefore the number of molecules of solvent in 1 c.c. of solution is

$$n_1 = \frac{w_1\rho_{12}}{M_1(w_1+w_2)}\times6{\cdot}23\times10^{23}. \quad . \quad . \quad . \quad \text{(l)}$$

Similarly

$$n_2 = \frac{w_2\rho_{12}}{M_2(w_1+w_2)}\times6{\cdot}23\times10^{23}, \quad . \quad . \quad . \quad \text{(li)}$$

M_2 being the molecular weight of the solute.

From (xxxvii) we have

$$S_{12}^{1/2} = \pm \frac{\sqrt{\pi}}{2\sqrt{6}} \left(\frac{c_1^{1/2} n_1}{\delta_1^{3/2}} + \frac{c_2^{1/2} n_2}{\delta_2^{3/2}} \right). \quad . \quad . \quad \text{(lii)}$$

Also from (ii) and (iii) we have

$$c_1^{1/2} = \frac{2\sqrt{6}}{\sqrt{\pi}} \cdot \frac{S_1^{1/2} \delta_1^{3/2}}{n}, \quad . \quad . \quad . \quad . \quad . \quad \text{(liii)}$$

where n corresponds to the number of molecules in the pure solvent and is given by the equation

$$n = 6{\cdot}23 \times 10^{23} \frac{\rho_1}{M_1}, \quad . \quad . \quad . \quad . \quad . \quad \text{(liv)}$$

ρ_1 being the density of the solvent.

Therefore from (lii) and (liii)

$$c_2^{1/2} = \pm \frac{2\sqrt{6}}{\sqrt{\pi}} \frac{\delta_2^{3/2}}{n_2} \left(S_{12}^{1/2} - \frac{n_1}{n} S_{11/2} \right). \quad . \quad . \quad \text{(lv)}$$

Substituting in (xlix), and writing

$$\delta_1 = \partial_1 \times 10^8,$$
$$\delta_2 = \partial_2 \times 10^8,$$

we get

$$p = 81{\cdot}84 \frac{w_1 M_2 T \lambda}{(w_1 M_2 + w_2 M_1)\phi_s} \times e^{-\frac{9{\cdot}665 M_1 S_1^{1/2} \{ S_1^{1/2} w_1 \rho_{12} (\partial_2^{1/2} - \partial_1^{1/2}) + S_{12}^{1/2} (w_1 + w_2) \rho_1 \partial_1 \}}{\rho_1^2 \partial_1 \partial_2^{1/2} \lambda^2 T (w_1 + w_2)}}; \quad . \quad . \quad . \quad \text{(lvi)}$$

or, if the solvent is associated,

$$p = \frac{81{\cdot}84 w_1 M_2 T \lambda}{(w_1 M_2 + w_2 A M_1)\phi_s} \times e^{-\frac{9{\cdot}665 A^{2/3} M_1 S_1^{1/2} \{ S_1^{1/2} w_1 \rho_{12} (\partial_2^{1/2} - A^{1/6} \partial_1^{1/2}) + S_{12}^{1/2} (w_1 + w_2) \rho_1 A^{1/6} \partial_1^{1/2} \}}{(w_1 + w_2) \rho_1^2 \partial_1 \partial_{12}^{1/2} \lambda^2 T}}. \quad . \quad . \quad . \quad \text{(lvii)}$$

In this equation ϕ_s is determined by the relation

$$\phi_s = v_{12} - \frac{\partial_{12}^3}{4}, \quad . \quad . \quad . \quad . \quad . \quad \text{(lviii)}$$

in which

$$v_{12} = \frac{M_{12}}{\rho_{12}},$$

M_{12} being the molecular weight of the solution and equal to

$$M_{12} = \frac{n_1 A M_1 + n_2 M_2}{n_1 + n_2},$$

giving

$$v_{12} = \frac{(w_1 + w_2) A M_1 M_2}{(w_1 M_2 + w_2 A M_1)\rho_{12}}, \quad . \quad . \quad . \quad \text{(lix)}$$

and ∂_{12} is the average of the nearest distances of approach of all the particles in the solution. This is determined as follows.

The number of encounters of the solvent molecules between themselves is proportional to n_1^2, those of the

TABLE

Vapour pressure at 18° of some salt solutions 100 grams of water making

	w_1.	w_2.	M_1.	M_2.	t.	ρ_1.	ρ_{12}.	v_s.	∂_1.
H_2O	—	—	18·02	—	18	0·9986	—	48·360	3·079
NaCl	100	17·64	18·02	58·46	18	0·9986	1·1087	44·725	3·079
NaI	100	17·64	18·02	149·92	18	0·9986	1·1269	42·702	3·079
KCl	100	17·64	18·02	74·56	18	0·9986	1·0978	46·445	3·079
KNO_3 ...	100	17·64	18·02	101·11	18	0·9986	1·0970	47·763	3·079
$AgNO_3$ ...	100	17·64	18·02	169·89	18	0·9986	1·1402	47·442	3·079

solute molecules among themselves to n_2^2, and those between the solvent and solute molecules to $2n_1n_2$. Therefore the average value of ∂_{12} is

$$\left(\frac{n_1 \partial_1^{1/2} + n_2 \partial_2^{1/2}}{n_1 + n_2}\right)^2$$

or

$$\partial_{12} = \left(\frac{w_1 A^{1/6} M_2 \partial_1^{1/2} + w_2 A M_1 \partial_2^{1/2}}{w_1 M_2 + w_2 A M_1}\right)^2 . \quad . \quad . \quad \text{(lx)}$$

In using this formula to calculate the vapour pressure of an aqueous solution, it must be borne in mind that the effect of dissolving a substance in water will be to alter

the cohesion of the liquid. It is possible, therefore, that the state of aggregation of the water molecules will be affected. In the absence of a means of determining this effect accurately it must be neglected, but it cannot be expected that the calculated values of the vapour pressure will be quite accurate. In Table III. the value of the association factor for water was taken throughout as 2·68, the value found for water at 18° as shown in Table II.

In this table the values of ∂ were calculated from the formula

$$\partial = \left(\frac{3{\cdot}24\mathrm{M}b}{2{\cdot}016}\right)^{1/3} \times 10^{-8}, \quad . \quad . \quad . \quad . \quad \text{(lxi)}$$

III.

containing 17·64 grams of salt dissolved in 15 per cent. solutions.

∂_2.	∂_s.	ϕ_s.	S_1.	S_{12}.	$K_{12} \times 10^{-8}$.	λ.	Vapour pressure in mm.	
							Calculated.	Observed.
—	—	31·94	72·66	—	67·75	1·568	15·7	15·5
3·789	4·232	25·772	72·66	77·41	73·16	1·579	12·1	13·63
4·304	4·299	27·835	72·66	74·03	68·88	1·568	14·1	14·93
4·148	4·283	26·796	72·66	76·00	70·97	1·575	13·1	14·1
4·382	4·308	27·813	72·66	74·40	69·12	1·569	13·7	14·6
4·148	4·292	27·675	72·66	74·70	69·67	1·571	14·07	—

which is probably more accurate than (xx); but, as the values obtained are slightly smaller, they were multiplied by 1·037 to bring them into line with those calculated from formula (xx), from which the values of λ had been deduced.

Considering the greater complexity of the conditions in mixed substances, it will be seen that the agreement between the observed and calculated values of the vapour pressures is fairly good. Actually the calculated values depend to an appreciable extent on the magnitude of the association factor A chosen for water. If this factor had been taken as 3·00, as suggested previously, with the corresponding values of λ, the vapour pressures of the solutions in Table III.

would work out at 13·56, 14·36, 13·53, 13·86, and 13·85 respectively.

These results must be regarded as preliminary only. It is important to be able to plot the $\lambda : K$ curve more accurately. The analysis is interesting, however, as indicating a new development of the kinetic theory that is capable of wide application, *e. g.*, to the viscosity of liquids, conduction of heat by liquids, the solution of liquids in liquids, etc. It is particularly noteworthy that the negative part of the $\lambda : K$ curve may correspond to the motion of negatively-charged particles, whose velocity must be less than that of moving particles not subject to the action of a repulsive force. As a particular case, an electron rotating in an orbit and passing near another electron at certain intervals of time, which may or may not be regular, would have its velocity retarded.

The general conclusion from these results is that moving particles of matter may not be treated as if they were isolated from the attractions and repulsions of adjacent particles: the definition of force requires that the velocities of such particles are affected by the action of the forces exerted on them by neighbouring particles or systems of forces, or, in other words, the law of equipartition of energy is not of general application.

Thus the mean kinetic energy of a mechanical system becomes

$$U = \tfrac{1}{2}\Lambda^2 kT \quad . \quad . \quad . \quad . \quad . \quad . \quad (lxii)$$

for each degree of freedom instead of $\frac{1}{2}kT$ as has been assumed previously; and if Λ is less than unity, the energy of such a system is less than $\frac{1}{2}kT$.

Returning to the particular case of the kinetic theory of solutions, it will be remembered that, in a previous paper *, it was shown that when the molecular fields of the solute and solvent are taken into account, the solubilities of substances generally, whether solid, liquid, or gaseous, can be accounted for, and that, when substances are arranged in the order of their solubilities, they are in the order of every other property of solutions, which, therefore, must also be due to the interaction of molecular forces.

In the same paper it was shown, in particular, that the observed increases in the depression of the freezing-point of aqueous solutions of salts below that due to a "normal" solute are caused by the enhanced cohesions of the solutions,

* Phil. Mag. xliv. p. 897 (1922).

resulting from the greater molecular fields of the solutes, and can be calculated from the surface tensions of the solutions.

In view of the analysis in the present paper, it will be seen that the basic assumption of the dissociation theory of solution, *i. e.*, that the reduction of the vapour pressure, elevation of the boiling-point, and depression of the freezing-point of solutions is proportional only to the number of molecules present, is incorrect. The observed values of these various properties of solutions are dependent partly on the fewer number of solvent molecules present, that is, on the number of solute molecules contained in the solution ; but they are also affected by the changes in volume and cohesion that are due to the added solute particles. When these additional factors are taken into consideration, the observed values of these properties are completely accounted for.

Instead, therefore, of being obliged to choose the " dissociation " of a substance in solution to fit the observed vapour pressure, etc., the properties of solutions can be calculated from the attractions of the particles and the densities of the liquids.

In this connexion it is interesting to calculate the actual forces of attraction between the particles in, *e.g.*, a 15 per cent. solution of potassium nitrate at 18°. If the molecules of potassium nitrate were dissociated, the force between the ions would be

$$f = \frac{(4{\cdot}7 \times 10^{-10})^2}{r^2}$$

$$= \frac{2{\cdot}21 \times 10^{-19}}{r^2} \text{ dyne.}$$

Supposing the ions to be 1×10^{-7} cm. apart, the force would be

$$f = 2{\cdot}21 \times 10^{-5} \text{ dyne.} \quad . \quad . \quad . \quad . \quad . \quad (a)$$

From (xl), (ii), and (li) we find that the observed surface tension of such a solution corresponds to an actual force between the molecules of potassium nitrate of

$$f = \frac{6{\cdot}24 \times 10^{-67}}{r^8} \text{ dyne}$$

or, at a distance of 1×10^{-7} cm., of

$$f = 6{\cdot}24 \times 10^{-11} \text{ dyne.} \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Thus the force between dissociated particles at this distance would be of the order of a million times as great, and would

decrease only in proportion to the square of the distance instead of to the eighth power. Measurement of the surface tension of the solution is sufficient to show that such forces do not exist within it.

In conclusion the writer wishes to express his indebtedness to Miss M. J. Humphries for much kind help with the somewhat laborious calculations.

Summary.

Maxwell's theory of the distribution of molecular velocities has been amplified to take into account the effect of molecular attraction. The extended theory has been applied to obtain expressions for the vapour pressures of a pure liquid and of a solution in terms of molecular attraction, motion, and volume only. The agreement between the calculated and observed values is so close as to indicate that the vapour pressures of liquids are actually dependent on these factors alone. This is particularly interesting in connexion with the theory of solutions, as it becomes unnecessary any longer to assume an hypothetical dissociation of salt molecules in solution to account for the greater reductions of the vapour pressures, depressions of the freezing-point, etc., of solutions of these substances.

The vapour pressure of a pure liquid is given by the formula

$$p = 81{\cdot}84\frac{T\lambda}{A\phi_s}\,e^{-\frac{9{\cdot}665MA^{2/3}}{T\vartheta\lambda^2\rho}},$$

and that of a solution by

$$p = 81{\cdot}84\frac{M_2w_1T\lambda}{(AM_1w_2+M_2w_1)\phi_s} \times e^{-\frac{9{\cdot}665A^{2/3}M_1S_1^{1/2}\{S_2^{1/2}\rho_{12}w_1(\vartheta_2^{1/2}-A^{1/6}\vartheta_1^{1/2})+S_{12}\rho_1(w_1+w_2)A^{1/6}\vartheta_1^{1/2}\}}{T\vartheta_1\vartheta_2^{1/2}\lambda^2\rho_1(w_1+w_2)}},$$

where

T is the absolute temperature;

λ is the ratio of the total average velocity of the molecules in the liquid under the given circumstances to that in a perfect gas;

A is the actual state of aggregation of the molecules in the given liquid;

ϕ is the co-volume of the liquid;

S its surface tension, the subscripts 1 and 2 indicating solvent and solute respectively ;

M its molecular weight ;

ρ its density ;

w_1 and w_2 the weights of solvent and solute in a solution ; and

$\partial \times 10^{-8}$ the nearest distance of approach of the centres of the molecules of the liquid.

It has been shown that the total average velocity of the molecules in a liquid cannot be the same as that in a perfect gas, for the reason that they are under the influence of strong forces. The ratio of these two velocities, λ, is dependent on the cohesion of the liquid, and the relation between λ and the cohesion K of the liquid has been shown to be determined by the equations

$$\left.\begin{aligned} K \times 10^{-8} &= 42{\cdot}16y - 64{\cdot}7y^3 + 952y^5, \\ \lambda &= 1 + y. \end{aligned}\right\}$$

Obviously the method is capable of wide application, and its success in this particular case indicates that the so-called classical dynamics may yet be found to be sufficient to explain phenomena for which, in the past, it had been supposed to be inadequate.

XVI. *The Corona Discharge in Nitrogen. By* L. G. H. Huxley, *M.A., D.Phil., Lecturer and Demonstrator at the Electrical Laboratory, Oxford* *.

IN a former paper † I have described experiments on the corona discharge in helium and neon, in which especial precautions were taken to secure the purity of the gas in the apparatus.

It was considered desirable to investigate also the corona discharge in a diatomic gas, and experiments which I have made with nitrogen are described below.

2. The apparatus was that used in the experiments on helium and neon, so that it is unnecessary to repeat in detail the description which has already been given (*loc. cit.*).

* Communicated by Prof. J. S. Townsend, F.R.S.

† Phil. Mag. v. p. 721, April 1928.

It consisted essentially of coxial cylindrical electrodes contained in a clear quartz envelope. The outer cylinder was a nickel tube 4·6 cm. in diameter and 12 cm. long, with guard-rings of the same diameter. The inner electrode was a nickel wire 1·65 mm. in diameter fixed along the axis of the outer tube by quartz supports.

Electrical connexions were made to the electrodes and guard-rings, and were brought through the quartz envelope by air-tight seals.

A second piece of apparatus was constructed identical with the first, with the exception of the central wire, which had a diameter of 3·16 mm.*

3. Pure nitrogen was obtained by heating pure sodium azide in a vacuum, and was stored in a glass flask.

To remove traces of mercury vapour the nitrogen passed through two traps cooled in liquid air, before entering the apparatus. The pressure of the gas was measured by a McLeod gauge from which mercury vapour was prevented from entering the apparatus by a third trap cooled in liquid air. The whole could be exhausted by a mercury vapour pump connected to the gauge, the arrangement being that used in the experiments on helium and neon.

Before making measurements it was necessary to drive impurities from the electrodes and the walls of the envelope. This was effected by introducing pure nitrogen into the apparatus and then heating the quartz to a high temperature with blow-pipes, at the same time passing a heavy discharge between the electrodes. The impurities which were evolved were removed with the nitrogen on exhausting the apparatus. This process was repeated many times, and when all impurities had been removed it was found that consistent results were obtained, which could be easily repeated.

In these experiments the gas was examined spectroscopically by means of a high-frequency discharge through the gas in the quartz tubes.

4. Measurements were then made of the potentials between the electrodes required to start discharges and to maintain currents through the gas over a range of pressures.

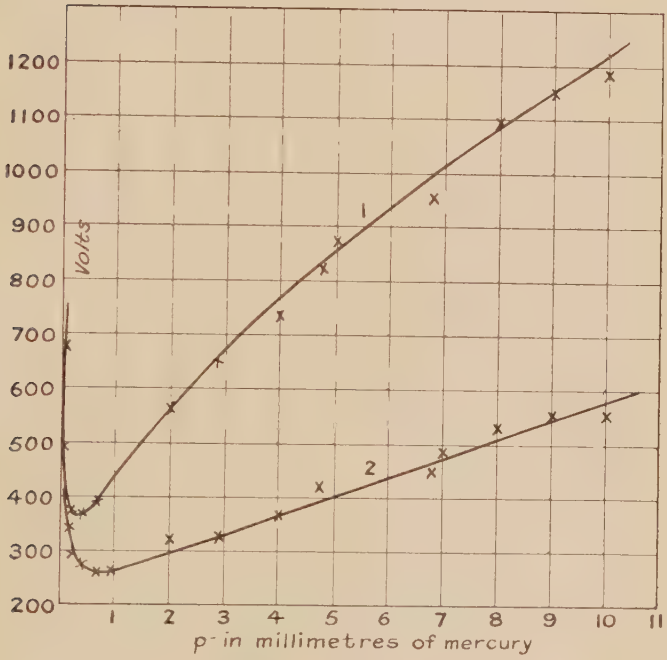
* In the experiments on the monatomic gases the wire was 2 mm. in diameter in the second apparatus. This was replaced by one of larger diameter.

The source of potential was a battery of small accumulators, and the potentials were measured by a standard voltmeter in series with a suitable resistance. The currents were measured by a sensitive galvanometer.

The results are most conveniently expressed in the form of curves, showing the potentials required to start a discharge as a function of the pressure of the gas.

The curves given in fig. 1 represent the results obtained

Fig. 1.



Starting potentials for wire 1·65 mm. diameter.
Curve 1. Wire positive.
„ 2. „ negative.

with the apparatus in which the wire (inner cylinder) was 1·65 mm. in diameter. Curve 1 gives the voltages required to start discharges when the wire was at a positive potential relative to the outer cylinder, and curve 2 the voltages when the wire was negatively charged.

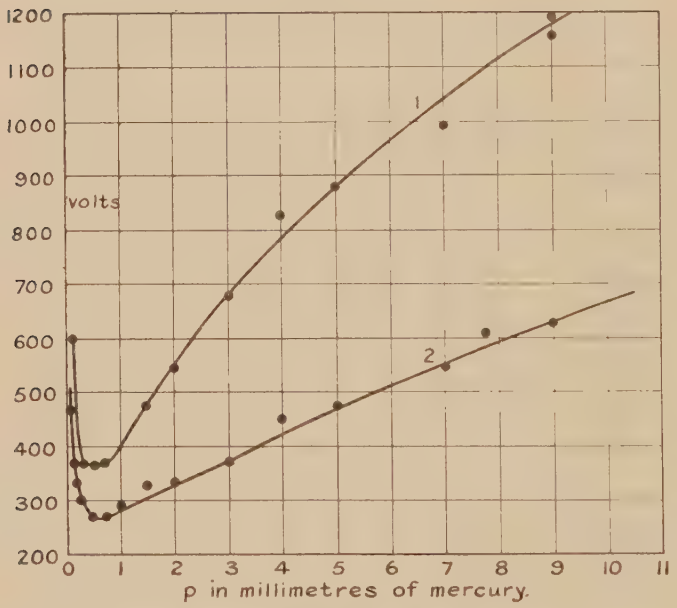
It will be seen that over the range of pressures investigated a discharge occurs more easily with the wire at a

negative potential than at a positive potential, and that both curves have well-defined minima.

In fig. 2 similar curves are given for the second apparatus (inner cylinder 3·16 mm. diameter).

5. The results of the experiments are in agreement with Townsend's theory *, which shows that in a corona discharge the following relation exists between the diameter

Fig. 2.



Starting potentials for wire 3·16 mm. diameter.
Curve 1. Wire positive.
„ 2. „ negative.

of the wire, the electric force X_1 at its surface, and the pressure p :—

$$aX_1 = f(ap)$$

provided the region of ionization in the gas does not extend to the outer electrode.

This is shown by the curve, given in fig. 3, showing the experimental values of the product aX_1 plotted as a

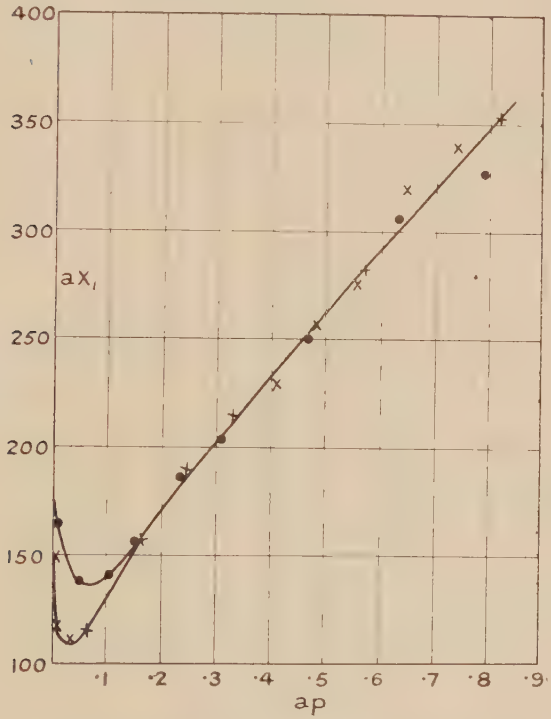
* ' Electricity in Gases,' p. 369.

function of the product ap for each apparatus for discharges in which the wires were at positive potentials.

The force X_1 is in volts per centimetre, a in centimetres, and p in millimetres of mercury.

The points corresponding to the smaller (1·65 mm.) and larger (3·16 mm.) values of a are indicated by crosses and circles respectively.

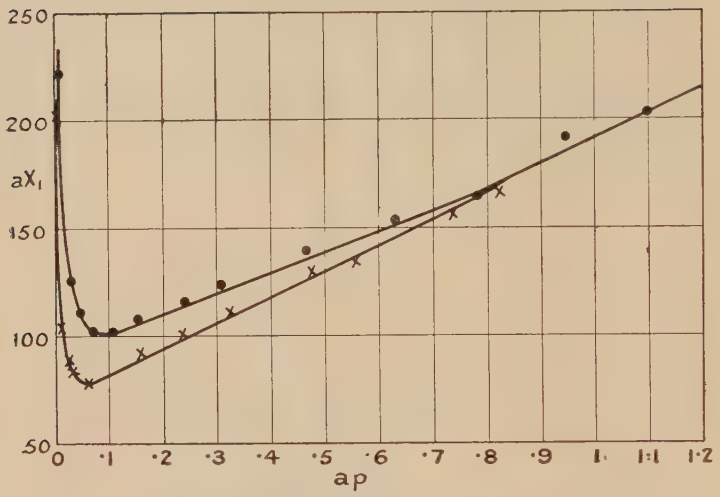
Fig. 3.



aX_1 as a function of ap wires positive,
Points marked X for wire 1·65 mm. diameter.
„ „ ⊙ „ 3·16 „ „

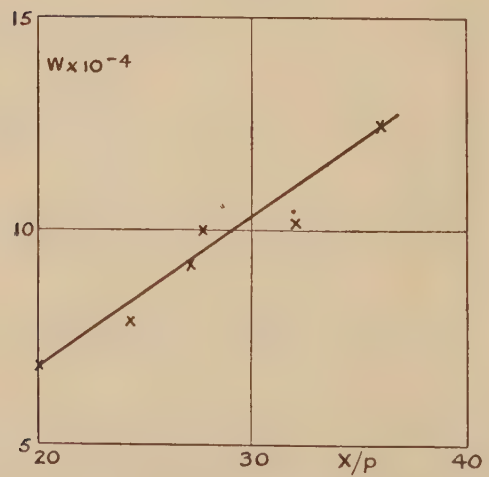
All the points lie on a single smooth curve, except at the minimum, where a divergence occurs. This indicates that at these pressures the region in which the gas is ionized extends to the outer electrode. In fig. 4 the corresponding results are shown for the wires when at negative potentials.

Fig. 4.



aX_1 as a functiou of ap wires negative.
Points marked X for wire 1·65 mm. diameter.
„ „ ⊙ „ 3·16 „ „

Fig. 5.



The velocities W, of positive ions in nitrogen in the direction of the electric force X_1 as a function of X/p.
W in centimetres per second, X in volts per centimetre, p in millimetres of mercury.

6. The velocities of the positive ions in the direction of the electric force were calculated from the potentials required to maintain various currents through the gas. The formula for the velocity in terms of the potential and the current has been given by Townsend *. This method is the same as that adopted in the experiments with monatomic gases †.

The velocities thus obtained for nitrogen are shown by the curve figure 5 for values of X/p from 20 to 36, being the average force in the space between the electrodes in volts per centimetre, and p the gas pressure in millimetres of mercury. The velocity W is given by the formula

$$W = 3{\cdot}5 \times 10^3 \times X/p.$$

If this formula held for small values of X/p the velocity under a volt per cm. in nitrogen at atmospheric pressure would be 4·6 cm. per sec.

XVII. *Diamagnetism and Sub-Molecular Structure.* *By* Francis W. Gray, *M.A., D.Sc., Senior Lecturer in Chemistry, Aberdeen University, and* John Farquharson, *B.Sc., Ph.D., Carnegie Research Scholar* ‡.

Van Vleck, Nat. Acad. of Sciences Proc. (Amer.) xii. pp. 662–670 (1926), by an application of the new quantum mechanics has derived an expression for the diamagnetic susceptibility of a gram atom.

L. Pauling, Roy. Soc. Proc. A, cxiv. pp. 181–211 (1927), has obtained the same expression, also by the aid of the new quantum mechanics. Pauling gives

$$\chi = \frac{-Ne^2}{6mc^2} \sum_{\kappa} \overline{r_\kappa^2}$$

(for S states and completed groups and subgroups), where

χ = the diamagnetic susceptibility of a gram atom,

N = Avogadro's number,

m = mass of an electron and e = its charge,

c = velocity of light,

* J. S. Townsend, Phil. Mag. (6) xxviii. p. 83 (1914).

† L. G. H. Huxley, *loc. cit.* p. 731.

‡ Communicated by the Authors.

r_κ = distance of the κth electron from the nucleus,

$\overline{r_\kappa^2}$ = time average of r_κ^2,

Σ_κ means that summation extends over all the electrons in the atom.

Further, wave mechanics gives an expression for $\overline{r_\kappa^2}$ in terms of the quantum numbers, and we have

$$\chi = -2{\cdot}010 \times 10^{-6} \Sigma_\kappa \frac{n_\kappa^4}{(Z - S_{M\kappa})^2} \left[1 - \frac{3l_\kappa(l_\kappa+1)-1}{5n_\kappa^2}\right],$$

where

n = total quantum number,

$l = k-1$ (where k = the old azimuthal number),

$S_{M\kappa}$ = screening number,

Z = charge of nucleus.

Pauling's method enables us to obtain theoretical values for the diamagnetic susceptibilities of free atoms or ions, and it is of very great importance that we should have such standard values for use in the interpretation of diamagnetic quantities observed in the laboratory. For a given nuclear charge and a given number of circum-nuclear electrons Pauling's value is the upper limit.

Any experimentally derived value, being obtained from substances in which the ions or atoms cannot be said to be free, must be less than Pauling's value and variable according to the nature of the substance, and therefore unsuitable as a standard. Such experimental values have hitherto been used as standards of reference, and this has been a most unsatisfactory feature of diamagnetic investigation.

We find, for example, that values for the atomic susceptibilities of the halogens have been given by Pascal and by Joos (Pascal, "L'additivité des propriétés diamagnetiques" (1913), and Joos, *Zeit. f. Phys.* xix. p. 347 (1923), and xxxii. p. 835 (1925).)

Pascal:—

	F.	Cl.	Br.	I.
Observed directly from elements ...	6·3	20·1 (Pascal)	30·6 (Pascal)	45·9 (Owan)
			30·6 (Honda)	44·4 (Honda)
Observed indirectly from compounds.	6·3 (Pascal)	19·3 (Pascal)	30·4 (Pascal)	44·6 (Pascal)

Joos:—

F^{-1}.	Cl^{-1}.	Br^{-1}.	I^{-1}.
10·8	19·5	38·3	57·5

The values by these two authorities agree, at least qualitatively, for the neutral atom, except in the case of chlorine, where either the value of Joos must be raised or that of Pascal must be lowered before complete consistence can be obtained.

All these numbers and other values for diamagnetism in this paper require to be multiplied by 10^{-6}.

Valency Bonds.

The present discussion deals with the relation of diamagnetism to two kinds of valency bonds.

1. *Covalency Bonds* such as we have in Cl_2, which may be regarded as

$$Cl^{+1}\,Cl^{-1} \quad \text{or} \quad Cl^{+1}-Cl^{+1},$$

where Cl^{+1} is Cl^{+7} surrounded by six electrons, and Cl^{-1} is Cl^{+7} surrounded by eight electrons (octet).

In $Cl^{+1}-Cl^{+1}$ the pair of electrons in the bond are shared by two octets and are in a state of oscillation to and fro between the two atoms, Cl^{+1} and Cl^{+1}, interchanging positions whereby there is a fluctuation of angular momentum.

In $Cl^{+1}Cl^{-1}$ the bond pair are both in the octet of Cl^{-1}, and only one of the constituent atoms has an octet.

There may be said to be a balance between the two conditions $Cl^{+1}Cl^{-1}$ and $Cl^{+1}-Cl^{+1}$.

The first condition represents a purely heteropolar molecule, the second a purely homopolar.

2. *Electrovalency Bonds* such as we have in KCl, which may be regarded as $K^{+1}Cl^{-1}$ or $K^{+1}-Cl^{+1}$, where K^{+1} is K^{+9} surrounded by eight electrons (octet), Cl^{-1} is Cl^{+7} surrounded by eight electrons (octet), and Cl^{+1} is Cl^{+7} surrounded by six electrons.

In $K^{+1}-Cl^{+1}$ the pair of electrons in the bond are not shared by two octets (unlike the case of Cl_2), but are in a state of oscillation to and fro between the two atoms K^{+1} and Cl^{+1} interchanging positions, whereby there is a fluctuation of angular momentum.

In $K^{+1}Cl^{-1}$ the bond pair are both in the octet of Cl^{-1} and both the constituent atoms have an octet.

There may be said to be a balance between the two conditions $K^{+1}Cl^{-1}$ and $K^{+1}-Cl^{+1}$.

The first condition represents a purely heteropolar molecule, the second a purely homopolar.

Octet formation for both atoms of the molecule is most readily obtained, on the one hand, with Cl_2 in the last

condition, *i. e.*, in $Cl^{+1}-Cl^{+1}$, and, on the other hand, with KCl in the first condition, *i. e.*, in $K^{+1}Cl^{-1}$.

Thus, the covalency bond favours the homopolar condition, the electrovalency bond the heteropolar.

The difference between the two types of bonds is more one of degree than of kind.

In the electrovalency bond one of the constituent atoms either contains a non-sharing octet, as K^{+1} in $K^{+1}-Cl^{+1}$, or no octet at all, as H^{+1} in $H^{+1}-Cl^{+1}$.

In the covalency bond both the constituent atoms either contain sharing octets, as in $Cl^{+1}-Cl^{+1}$, or no octets at all, as in $H^{+1}-H^{+1}$.

In this view of a single bond, of whatever type, there are always concerned two electrons, which may be called simply valency electrons.

Some molecules contain both types of bonds, *e. g.*,

		Bonds.	
H_2O_2	Hydrogen-oxygen.	Electrovalency.	More heteropolar.
	Oxygen-oxygen.	Covalency.	More homopolar.
$KClO_3$ ...	Potassium-oxygen.	Electrovalency.	More heteropolar.
	Chlorine-oxygen.	Covalency.	More homopolar.

The activation of covalency produces a greater depression of diamagnetism (greater fluctuation of angular momentum) than the activation of electrovalency.

It is usually easy formally to represent a diamagnetic molecule as derived from a neutral group of ions—that is, a group of positive and negative ions for which the algebraic sum of the charges is zero.

In the present discussion we consider the diamagnetic changes brought about by the coming closer together of the widely separated ions of the *neutral group* first to form *the molecule*, and afterwards, by an imaginary forced merging of the ionic nuclei, to form a single *merger atom*.

For example, the *neutral group* $K^{+1}+Cl^{-1}$ gives *the molecule* KCl and the *merger atom* Kr.

As the inner levels of the neutral group are completely filled, the formation of the merger atom involves the raising of the quantization of several of the electrons with a corresponding rise of diamagnetism. On the other hand, this rise is counteracted by a fall due to the larger nucleus of the merger atom, the result being that the final diamagnetism *may* differ little from the original value. For example:

$$K^{+1}+Cl^{-1}=45{\cdot}7, \quad Kr=42,$$
$$K^{+1}+Br^{-1}=70{\cdot}7, \quad Xe=66.$$

Similar results may be obtained from a neutral group containing neutral atoms. For example :

$$2A = 43{\cdot}0, \quad Kr = 42,$$
$$A + Kr = 63{\cdot}5, \quad Xe = 66.$$

There are cases, however, where the difference is considerable. For example :

$$3H^{+1} + N^{-3} = 22 \quad \text{and} \quad Ne = 5{\cdot}7.$$

Here the circumnuclear electrons in N^{-3} and Ne are the same in number, configuration, and quantization. The lower diamagnetism in Ne is due entirely to the amount by which the nuclear charge in Ne is greater than in N^{-3}.

Similarly for

$$4H^{+1} + C^{-4} = 50 \quad \text{and} \quad Ne = 5{\cdot}7.$$

For the purpose of the present paper it is of special interest to examine the relation of the experimental molecular diamagnetism to the theoretical values for the neutral group, on the one hand, and for the merger atom on the other.

When the ions only approach near enough to one another to give the molecule any change in diamagnetism may be regarded as taking place mainly in the outer layers, the inner layers remaining almost unchanged.

The diamagnetism of a diatomic molecule is the resultant of three parts :—(1) the diamagnetism of electrons under the influence of one nucleus, (2) the diamagnetism of electrons under the influence of the other nucleus, (3) the diamagnetism and weak paramagnetism of electrons under the influence of both nuclei. The first two parts form the diamagnetism of the unchanged cores ; the third part is the magnetism of the remaining or surplus or valency electrons, any one of which does not belong to one nucleus more than to the other, but may be said to be influenced by a virtual nucleus which lies between the real nuclei and is the vector sum of these.

Thus in a diatomic molecule there are in general three nuclei (two real and one virtual).

In the formation of the molecule from the ionic group, then, if there is no rise of quantization, any change in diamagnetism should be in the direction of a depression, and this conclusion is supported by experimental results. This depression, according to its amount, may be attributed (1) to the distortion of the electronic orbits, or (2) to the

activation of valency together with distortion. The distortion loss may be regarded as small compared with the valency loss.

The valency loss is of two-fold origin. It is partly due to the amount by which the virtual nucleus is greater than either of the real nuclei, and partly to the development of a weak form of paramagnetism independent of temperature. This paramagnetism may be explained by the fluctuation of angular momentum arising from the interchange occurring in the Heitler-London activation of valency.

In this view, when a diatomic molecule is being formed, we see a virtual nucleus assuming control over certain of the electrons originally controlled by only one or the other of the two real nuclei, and along with this there is the development of weak paramagnetism.

According to the amount of the diamagnetic depression different molecules show different stages in the development of this new control. The virtual nucleus is building up a set of levels of its own. We have in the molecule the first beginnings of a gradual growth, round the virtual nucleus, of a structure which finally culminates in the merger atom in which the virtual nucleus has become real. In the earlier stages of this development the new structure consists of electrons derived from the outer layers of the original atoms or ions with diamagnetic depression. In the later stages, however, after the supply of electrons from the outer layers of the original atoms has become exhausted, the new growth takes place at the expense of electrons from inner layers, and a point is reached where there must be a rise of quantization with a corresponding rise of diamagnetism. This diamagnetic rise cancels part of the depression of the earlier stages and also part of the depression due to the amount by which the virtual nucleus exceeds either of the real nuclei. In the course of this process, therefore, the diamagnetism first falls down to a minimum and then rises, and ultimately, when the merger atom is formed, attains a value that may not differ much from the original.

We expect, then, the molecular diamagnetism to be always less than that of the neutral group, and to be sometimes less than that of the merger atom also. A very great depression usually brings the molecular diamagnetism below that of the merger atom, and in any case points to great fluctuation of angular momentum and a decidedly homopolar nature.

In the case of methane the diamagnetic depression is so great that there is indicated a large interchange effect and

homopolar character. In passing from the molecule to the merger atom, there is involved a diamagnetic rise due to a rise of quantization and a diamagnetic fall due to a rise in the nuclear charge. The latter effect must be greater than the former, since methane lies diamagnetically between the neutral group and the merger atom. The diamagnetic difference between $4H^{+1}+C^{-4}$ (50) and Ne (5·7) shows that in this case the diamagnetic depression due to rise of nuclear charge is very great.

Table I. (p. 198) contains numerical values illustrating the above discussion.

In the paper mentioned above Pauling has given diamagnetic susceptibilities for sets of ions having the same number of circumnuclear electrons as He, Ne, A, Kr, Xe, and Cu^{+1}, Ag^{+1}, Au^{+1}. But, in addition to these, we require ions for which the number of circumnuclear electrons is different from any of Pauling's numbers, and it is important to inquire to what extent these other ions are suitable for the interpretation of molecular diamagnetism.

In a recent paper (Phys. Rev. xxxi. p. 587, 1928) Van Vleck has developed an expression for atomic susceptibility which may be put simply thus : —

$$\chi = P_x + P_y - D,$$

where D is the pure diamagnetism the expression for which is that given by Pauling.

P_x is paramagnetism dependent on temperature, the value for which is large compared with P_y or D ; and P_y is a weak form of paramagnetism, independent of temperature.

The constituent groups of circumnuclear electrons present in Pauling's ions are in every case complete, consisting of two *s* electrons, six *p* electrons, ten *d* electrons, or fourteen *f* electrons. Each of these completed groups gives a $^1S_0$ state, and therefore displays pure diamagnetism. The value of the resultant spin and that of the resultant orbital angular momentum are both zero; therefore the paramagnetic moment is zero and $P_x=0$. Also, there is no fluctuation of angular momentum to give any P_y. Accordingly, Pauling's expression for D gives the atomic susceptibility, and Pauling's values are admissible as standards to be used in the interpretation of molecular diamagnetism.

In the case of Pauling's ions the spin and the orbital angular momentum are *both* zero, but a zero value for P_x may be obtained under certain conditions when the *resultant* of the spin and the angular momentum is zero, *i. e.*, when

$J=0$. This may be the case with sub-groups containing two p electrons, four d electrons, and six f electrons. These

Table I.

The Diamagnetism of

the neutral group of widely separated ions.		*the molecule* obtained by combining the ions.		*the merger atom* obtained by an imaginary forced merging of the nuclei.	
$H^{+1}H^{-1}$	8				
or H^0+H^0	4·83	H_2	4·71	He	1·54
$2H^{+1}-O^{-2}$	12·6	H_2O	12·96	Ne	5·7
$3H^{+1}+N^{-3}$	22	NH_3	17·05	Ne	5·7
$4H^{+1}+C^{-4}$	50	CH_4	12·2	Ne	5·7
$2H^{+1}+O^{-2}+O^0$	19·79	H_2O_2	16·73	A	21·5
$H^{+1}+Cl^{-1}$	29	HCl	23·05	A	21·5
$H^{+1}+Br^{-1}$	54	HBr	31·45	Kr	42
$H^{+1}+I^{-1}$	80	HI	49·29	X	66
$K^{+1}+Cl^{-1}$	45·7	KCl	36·15	Kr	42
$K^{+1}+Br^{-1}$	70·7	KBr	48·12	X	66
$K^{+1}+I^{-1}$	96·7	KI	63·9	(Hf	87)
$4H^{+1}+N^{-3}+Cl^{-1}$	51	NH_4Cl	35·71	Ni	15
$4H^{+1}+N^{-3}+Br^{-1}$	76	NH_4Br	46·71	Pd	52
$4H^{+1}+N^{-3}+I^{-1}$	102	NH_4I	69·48		
$K^{+1}+Cl^{+5}+3O^{-2}$	60·21	$KClO_3$	40·7		
$K^{+1}+Br^{+5}+3O^{-2}$	68·24	$KBrO_3$	52·3		
$K^{+1}+I^{+5}+3O^{-2}$	82·18	KIO_3	63·1		
$H^{+1}+I^{+5}+3O^{-2}$	65·48	HIO_3	50·41		
$K^{+1}+Cl^{+7}+4O^{-2}$	68·3	$KClO_4$	44·6		
$K^{+1}+I^{+7}+4O^{-2}$	84·1	KIO_4	72		
$H^{+1}+I^{+7}+4O^{-2}$	67·4	HIO_4	56·55		
$2I^{+5}+5O^{-2}$	118·36	I_2O_5	79·4		
$I^{+1}+Cl^{-1}$	86·27	ICl	54·54		
$I^{+3}+3Cl^{-1}$	127·53	ICl_3	90·16		

yield various possible terms, the lowest of which are multiplets of which the triplet $^3P_{0,\,1,\,2}$ in the p sub-group is an example. In each case the multiplet is normal and the deepest component is that with J equal to zero.

If the multiplet interval is large, it is possible to deal with

each component separately, and the normal state is that with $J=0$, for which $P_x=0$ being equal to

$$Ng^2J(J+1)\beta^2/3kT,$$

where β is a Bohr magneton and the other letters have the usual significance. On the other hand, P_y does not vanish, and with these quotas of electrons the atomic diamagnetism is a value calculated by Pauling's method, but diminished by an amount equal to P_y.

Again, if the multiplet interval is narrow, the components cannot be considered separately and P_x does not vanish, being equal to

$$N[4S(S+1)+L(L+1)]\beta^2/3kT,$$

where S is the resultant spin,

L is the resultant angular momentum,

and β is a Bohr magneton.

On the other hand, some of the ions specially interpolated for the purpose of the present discussion do contain sub-groups that yield, in their deepest state, values for J differing from zero. Of these doubtful sub-groups some seem to have little claim to consideration, whilst for others, where the multiplet component separation is wide, the possibility should be kept in mind that they may be in a state somewhat higher than the deepest. This possibility should be considered in connexion with those sub-groups containing quotas complementary to the quotas two p, four d, and six f electrons, namely, four p, six d, and eight f electrons. These give the same multiplets in their stable state as the complementary quotas, but inverted. The deepest state does not give J equal to zero.

Accordingly, for the widely separated atoms or ions of the neutral group, i. e., *before the formation of the molecule,* Pauling values for the atomic diamagnetism may be used for a $^1S_0$ state without any correction, but when there is a multiplet and $J=0$, then, although Pauling's values may still be used, they should be subjected to a reduction.

On the other hand, *after the formation of the molecule* all the atomic diamagnetisms are subject to a depression, whether the free atoms and ions are in $^1S_0$ or in multiplet states, and even when the molecule is in a $^1\Sigma$ state.

It is the object of the present research to investigate this depression, which is partly due to fluctuation of angular momentum.

In the present discussion the following values from Pauling's paper are utilized :—

F^{-1}	Cl^{+7}	Cl^{-1}	Br^{+7}	Br^{-1}	I^{+7}	I^{-1}
8·1	1·2	29	6·0	54	17	80

O^{-2}	N^{+5}	N^{-3}	C^{+4}	C^{-4}
12·6	0·11	22·0	0·15	50

Na^{+1}	K^{+1}	Rb^{+1}
4·2	16·7	35

H^{-1}	H^{0}
8	2·415

It is assumed that the atomic susceptibility of H^{+1} is zero. In the treatment of halogen compounds, however, values are required for the valency stages $+1$, $+3$, and $+5$, in addition to the stages -1 and $+7$ given above, between which it has been necessary for us to interpolate the three missing quantities. We remove the two outermost electrons in I^{-1} to obtain I^{+1}. To calculate the smaller diamagnetism of the new ion we must not assume that the core, from which the outermost pair is detached, is the same as the ion I^{+1}, formed after the pair is removed. When the core changes to the new ion the orbits shrink to smaller dimensions. Accordingly, to obtain the diamagnetism of I^{+1} we must adopt one of two courses. We may calculate the diamagnetism of the pair, using a larger screen-number than that assigned to the pair when part of I^{-1}, and subtract the diamagnetism so obtained from the value for I^{-1}; or we may calculate I^{+1} afresh, using for each layer screen-numbers less than those assigned to I^{-1}. The values shown below have been obtained by the first method.

In order to work out the values it is necessary to have suitable screening numbers. For the ion with charge -1 Pauling gives only two screening numbers for the four outer pairs of electrons—one for the three pairs with azimuth number 2, and one for the single pair with azimuth number 1. In the process of stripping the electrons away a pair at a time to get the successive steps already referred to, use has been made here of four screening numbers, one for each of the steps

$$-1 \rightarrow +1 \rightarrow +3 \rightarrow +5 \rightarrow +7.$$

Both the susceptibility of the pair removed and the corresponding screening number must diminish as the

process proceeds. By keeping these requirements in view, and using Pauling's screening numbers as a guidance, it has been possible to carry out the required interpolations.

The method has been applied to other atoms in addition to the halogens. Some of the results are shown in Tables II., III., and IV.

TABLE II.

Diamagnetic increment obtained when a pair of electrons is added to the given ion to yield the ion to the right. Below each diamagnetic increment is placed the Hund symbol for the layer in which the pair is situated.

C^{+4}	C^{+2}	C^{0}	C^{-2}	C^{-4}
4·68	5·50	10·68	29	
2*s*	2*p*	2*p*	2*p*	
N^{+5}	N^{+3}	N^{+1}	N^{-1}	N^{-3}
2·93	3·15	5·27	10·54	
2*s*	2*p*	2*p*	2*p*	
O^{+6}	O^{+4}	O^{+2}	O^{0}	O^{-2}
2·01	2·00	3·10	5·41	
2*s*	2*p*	2*p*	2*p*	
F^{+7}	F^{+5}	F^{+3}	F^{+1}	F^{-1}
1·46	1·42	2·03	3·12	
2*s*	2*p*	2*p*	2*p*	
Cl^{+7}	Cl^{+5}	Cl^{+3}	Cl^{+1}	Cl^{-1}
4·51	5·21	7·27	10·81	
3*s*	3*p*	3*p*	3*p*	
Br^{+7}	Br^{+5}	Br^{+3}	Br^{+1}	Br^{-1}
7·74	9·35	12·72	18·19	
4*s*	4*p*	4*p*	4*p*	
I^{+7}	I^{+5}	I^{+3}	I^{+1}	I^{-1}
10·68	12·85	16·74	22·74	
5*s*	5*p*	5*p*	5*p*	

Magnetism of Valency Electrons.

Table II. shows the increment of diamagnetism when a pair of electrons is added to any given ion to obtain an ion with two more circumnuclear electrons.

Table III. shows the effective nucleus acting on each electron of the pair referred to.

We have the following relationships between the diamagnetic increments and between the effective nuclei.

In passing down a column of the diagram for C, N, O, F, we see that the quantum numbers of all the pairs of electrons are the same and the diamagnetism of the pair diminishes,

Table III.

Effective Nucleus.

Each electron of the pair of electrons added to the given ion to obtain the ion to the right is acted on by the effective nucleus shown below.

C^{+4}	C^{+2}	C^{0}	C^{-2}	C^{-4}
3·8	2·96	2·12	1·29	
N^{+5}	N^{+3}	N^{+1}	N^{-1}	N^{-3}
4·8	3·91	3·03	2·14	
O^{+6}	O^{+4}	O^{+2}	O^{0}	O^{-2}
5·8	4·91	3·95	2·98	
F^{+7}	F^{+5}	F^{+3}	F^{+1}	F^{-1}
6·8	5·82	4·87	3·93	
Cl^{+7}	Cl^{+5}	Cl^{+3}	Cl^{+1}	Cl^{-1}
8·59	7·45	6·31	5·17	
Br^{+7}	Br^{+5}	Br^{+3}	Br^{+1}	Br^{-1}
11·60	10·16	8·72	7·28	
I^{+7}	I^{+5}	I^{+3}	I^{+1}	I^{-1}
15·4	13·7	12·0	10·3	

and collateral with this there is an increase in the effective nucleus.

For example :—

	C^{+2}.	N^{+3}.	O^{+4}.	F^{+5}.
Diamagnetic increments	5·495	3·15	2·003	1·223
Hund symbol for pair of electrons ...	$2p$.	$2p$	$2p$	$2p$
Effective nucleus	2·96	3·91	4·91	5·82

If we add to the given ion not only a pair of electrons but also a positive ion, then the diamagnetism of the pair (which now may be called valency diamagnetism) will be less than before, but the relative order of the values will remain the same as in Table II.

Table II. provides a means of estimating the change in diamagnetism caused by a change in valency bonds. For example, if two N^{+3} valency bonds (each containing two

TABLE IV.

Ionic Diamagnetic Susceptibilities.

C^{+4}	C^{+2}	C^{0}	C^{-2}	C^{-4}
0·15	4·83	10·32	21·00	50
N^{+5}	N^{+3}	N^{+1}	N^{-1}	N^{-3}
0·11	3·04	6·19	11·46	22
O^{+6}	O^{+4}	O^{+2}	O^{0}	O^{-2}
0·08	2·09	4·09	7·19	12·6
F^{+7}	F^{+5}	F^{+3}	F^{+1}	F^{-1}
0·063	1·52	2·95	4·98	8·10
Cl^{+7}	Cl^{+5}	Cl^{+3}	Cl^{+1}	Cl^{-1}
1·20	5·71	10·92	18·19	29·0
Br^{+7}	Br^{+5}	Br^{+3}	Br^{+1}	Br^{+1}
6·00	13·74	23·09	35·81	54·00
I^{+7}	I^{+5}	I^{+3}	I^{+1}	I^{-1}
17·00	27·68	40·53	57·27	80·00

electrons) are changed to three N^{+5} valency bonds, then there is an increase of diamagnetism amounting to

$$(2\cdot93+3\cdot15+5\cdot27)-(3\cdot15+5\cdot27)$$

or 2·93 diminished by an amount depending on the atom sharing the bond with nitrogen, and by an amount depending on the interchange effect.

In the diagram for F, Cl, Br, and I there is an important difference from C, N, O, and F.

In passing down a column of the F, Cl, Br, I diagram, the level of the electronic pair rises, with the result that,

although the increasing effective nuclei should cause a diminishing diamagnetic increment, yet the increasing quantum numbers bring about a predominating increase in the increment. Accordingly, in passing down a column of the diagram for F, Cl, Br, and I there is (contrary to what we see with C, N, O, F) an increasing diamagnetic increment and a corresponding increasing valency diamagnetism.

In the case of some substances, such as ammonia, the difference between the diamagnetism of the neutral group and that of the molecule is not great enough to warrant the assumption of much loss from the interchange effect, and the depression is to be ascribed mostly to increase of the effective nucleus. On the other hand, there are substances such as methane where the depression is so great that it cannot be explained without a large fluctuation of angular momentum due to the interchange effect.

In selecting suitable ions, account has to be taken not only of the electronic groups within the ions themselves, but also of the interionic valency groups containing the surplus electrons, and in doubtful cases preference should be given to groups the quotas of which are suitable with respect to their values for resultant spin and resultant orbital angular momentum.

Of the ions or atoms given in Table IV., all have zero values for these quantities except those in columns 3 and 4. Those in column 3, C^{0}, N^{+1}, O^{+2}, F^{+3}, Cl^{+3}, Br^{+3}, and I^{+3}, if the multiplet intervals are assumed wide enough, have zero value for J, *i. e.* for the resultant of the spin and the orbital angular momentum, and the atomic susceptibility is that given by the Pauling formula diminished by an amount due to high-frequency paramagnetism.

In the ions in column 4, *i. e.* those next to the last in each row, namely C^{-2}, N^{-1}, O^{0}, F^{+1}, Cl^{+1}, Br^{+1}, and I^{+1}, the incomplete outer shell is a p layer containing four electrons, and therefore complementary to the non-paramagnetic quota of two electrons. These ions will, therefore, in the isolated state display paramagnetism unless they are considered to be in a state somewhat higher than the deepest.

In studying each diamagnetic molecule, the procedure adopted in the present paper is to consider the suitability of various trial structures. The constituent parts of each structure are ions or cores selected from the list given above.

A structure may be rejected because the number of surplus electrons is unsuitable for distribution among the bonds, or because theoretically a paramagnetic moment has to be

assigned to the outer group of one or more of the constituent cores.

The first structure to be studied in each case is that containing the ions of the neutral group. The amount by which the molecular diamagnetism is less than that of the neutral group gives some indication of the homopolar character of the substance. Then a structure is considered containing smaller ions than those of the neutral group, and the magnetism is estimated of the surplus or valency electrons, two of which are assigned to each bond. A compound may contain both homopolar and heteropolar bonds. The first show small diamagnetism or, it may be, paramagnetism; the second show less reduced diamagnetism.

The diamagnetism of an ion when acting as a core is somewhat larger than when in the isolated state. Again, the above strictures regarding the paramagnetism of certain ions refer to isolated particles, and certain ionic values are used in this discussion to which exception might be taken if the ions were isolated.

Applications of the above Theory.

Water and Ammonia.

Trial structure.	Theoretical sum of ionic diamagnetisms.	Experimental molecular susceptibility.	Number of surplus electrons.	Diamag. of surplus electrons.
$2H^{+1}+O^{-2}$	12·6	12·96	0	(0·36)
$2H^{+1}+O^{0}$	7·19	.....	2	5·77
$2H^{+1}+O^{+2}$	4·09	.....	4	8·87
$3H^{+1}+N^{-3}$	22	17·05±0·41	0	−5
$3H^{+1}+N^{-1}$	11·46	.....	2	5·59
$3H^{+1}+N^{+1}$	6·19	.....	4	10·86
$3H^{+1}+N^{+3}$	3·04	.....	6	14·01

For water the given experimental figure is the very reliable and generally accepted value, and for ammonia the value measured by Farquharson using strong aqueous solutions. The value for ammonia gas in agreement with this would be about 18, whereas 19 is usually given.

Water is quite exceptional in having an experimental molecular susceptibility that shows no depression below that of the neutral group. There is a very slight rise instead. Water has been so thoroughly investigated experimentally

that doubt seems to be suggested rather regarding the theoretical value of O^{-2}, which is probably too low. In any case, should there turn out to be really a depression in the case of water, then it seems likely that this depression would be small compared with that in ammonia, which again shows a much smaller depression than methane. The very great lowering in methane, which is confirmed by methyl substitution products, indicates that the fluctuation of angular momentum in the interchange process has a far greater effect in methane than in ammonia or water, where any depression is mainly due to change of effective nucleus.

The structure suggested for water contains oxygen in the form O^{+2}, which is assigned the value 4·09, which, however, should be subjected to a reduction, as explained above. If this is done, the exceptional character of water is made still more marked.

The second structure in water and the second and third in ammonia are rejected because there are not enough surplus electrons for the bonds.

The two bonds in water require at least four valency electrons, *i. e.* two for each bond ; similarly, ammonia requires at least six valency electrons, two for each of its three bonds. The second structure in each case also receives less favour for another reason : theory assigns a paramagnetic moment to both O^0 and N^{-1} in the isolated condition, unless in a state somewhat higher than the lowest.

On the other hand, ions with larger positive charges than those shown in the above table would give unnecessarily large numbers of surplus electrons. Accordingly, the most suitable structures seem to be $2H^{+1}+O^{+2}$ for water and $3H^{+1}+N^{+3}$ for ammonia. The valency diamagnetism is then 8·87 in water and 14·01 in ammonia. These values may be compared with the increments $3·098+5·412$ or 8·15 for O^{+2} and $3·15+5·27+10·54$ or 18·96 for N^{+3} (see Table II.).

The suggestion has sometimes been made that for a molecule the atoms of water are at the corners of a triangle and not in one straight line, the atoms of ammonia at the corners of a tetrahedron, and the atoms of methane at the corners of a pyramid with four-sided base. This suggestion is favoured by considerations of dielectric capacity and other properties.

In the present structure, there is a single bond (corresponding to a pair of electrons) in each of two of the sides of the water triangle, the third side being unoccupied,

and there is a single bond in each of three of the edges of the ammonia tetrahedron, the other three edges being unoccupied.

The above structures for water and ammonia have octets round the oxygen and nitrogen atoms, some of the electrons of the octet forming bonds.

Hydrogen Peroxide.

The experimental molecular diamagnetism of hydrogen peroxide is $16{\cdot}73 \pm 0{\cdot}20$ (measured in this laboratory by Farquharson).

If an octet is supposed to be round each oxygen atom, the choice for hydrogen peroxide seems to be between two structures, for which the following are the diamagnetic details :—

Diamagnetisms.

	Cores.	Three bonds.	Two H—O bonds.	One O—O bond.	Average of two H—O bonds.
$O^{+2}-O^{+2}$ $\vert \quad \vert$ $H^{+1} \quad H^{+1}$	8·18	8·55	6·20	2·35	3·10
H^{+1} $\diagdown$ $O^{+4}-O^{0}$ $\diagup$ H^{+1}	9·28	7·45	5·10	2·35	2·55

When the two H—O bonds are attached to *different* O^{+2} cores, the bond magnetisms are given by $3{\cdot}1+3{\cdot}1$ or $6{\cdot}2$ (see Table II.), subjected to appropriate reduction. When they are attached to the *same* O^{+4} core, the values are given by $2{\cdot}00+3{\cdot}10$ or $5{\cdot}10$, subjected to appropriate reduction. Although the O—O bond works out as the same for both structures, the first formula receives the greater support from the present measurements because, by it, it is clearer that the H—O bond is more heteropolar than the O—O bond.

In the above no reduction has been made in the diamagnetic increments of Table II. Probably any required reduction would be slight, but, even so, it would go to diminish still further the diamagnetic difference between the two kinds of bonds.

As pointed out already, from the fact that water appears not to show a depression below the neutral group, we conclude that the given theoretical value of the atomic susceptibility of O^{-2} is probably too low. If it were higher,

water would show a depression, and in hydrogen peroxide the difference between the two kinds of bonds would be more distinct.

The first arrangement shown above suits the dielectric capacity better than a structure with all four ions in the same straight line: $H^{+1}-O^{+2}-O^{+2}-H^{+1}$.

Again, hydrogen peroxide is not formed by the oxidation of water, but by the reduction of oxygen. So it must not be thought that the molecular structure of hydrogen peroxide can be built up by merely taking the water triangle (having $2H^{+1}$ and O^{+2} at the three corners) and attaching an oxygen atom to the outside of the O^{+2} corner. A more suitable and a simpler structure is the one given above, which also agrees with the formation of peroxides such as BaO_2.

The Chloride, Bromide, and Iodide of Ammonium.

The following molecular diamagnetisms were determined by Farquharson:—

NH_4Cl.	NH_4Br.	NH_4I.
$35{\cdot}71\pm0{\cdot}47$	$46{\cdot}71\pm0{\cdot}36$	$69{\cdot}48\pm0{\cdot}22$

NH_3.	HCl.	HBr.	HI.
$17{\cdot}05\pm0{\cdot}41$	$23{\cdot}05\pm0{\cdot}20$	$31{\cdot}45\pm0{\cdot}15$	$49{\cdot}29\pm1{\cdot}36$

The values for the salts were determined from measurements on the solids, and those for ammonia and the hydrogen halides from very concentrated aqueous solutions. The value for ammonia gas in agreement with the above would be about 18, and that for hydrogen chloride gas about 24·2, whereas the value usually given for ammonia gas is 19 and that calculated for hydrogen chloride gas by Mott Smith from argon and Cl^{-1} is 24·65 (Phys. Rev. xxxii. p. 821, 1928).

The confirmation thus obtained for the above values for NH_3 and HCl from concentrated solutions, and the small experimental errors, encourage us to place in these numbers a confidence which may reasonably be extended to those for HBr and HI also.

For each of the above the molecular diamagnetism is less than the value for the corresponding neutral group, the following depressions being shown:—

NH_3.	HCl.	HBr.	HI.
4·95	5·95	22·55	30·71

A further diamagnetic change appears when ammonia and hydrogen halide unite to form ammonium halide :—

	$NH_3+HCl\rightarrow NH_4Cl.$	$NH_3+HBr\rightarrow NH_4Br.$
Loss.....	4·39	1·79

	$NH_3+HI\rightarrow NH_4I.$
Gain	3·14

By adding together the appropriate losses we obtain the total depression displayed on the formation of each salt :—

NH_4Cl 15·29, NH_4Br 29·29, NH_4I 32·52.

When the total depression is large the greater part occurs in the formation of hydrogen halide, only a small change occurring in the formation of ammonia and in the union of ammonia and hydrogen halide.

The very large depressions in HBr and HI, and the small ones in HCl and NH_3, indicate a large interchange effect and homopolar nature in HBr and HI, and a small interchange effect and more heteropolar nature in HCl and NH_3. This explanation also surmounts a difficulty encountered if we ascribe similar structures to all the hydrogen halides and try to reconcile the molecular diamagnetisms.

The diamagnetic data may be explained by representing the reactions thus :—

	Core change.	Valency change.	Net result.
$H^{+1}_{H^{+1}}\!\!>\!N^{+3}+H^{+1}-Cl^{+1}\rightarrow H^{+1}_{H^{+1}}\!\!>\!N^{+5}-H^{+1}-Cl^{+1}$	fall 2·93	fall 1·46	fall 4·39
$H^{+1}_{H^{+1}}\!\!>\!N^{+3}+H^{+1}-Br^{+1}\rightarrow H^{+1}_{H^{+1}}\!\!>\!N^{+5}-H^{+1}-Br^{+1}$	fall 2·93	rise 1·14	fall 1·79
$H^{+1}_{H^{+1}}\!\!>\!N^{+3}+H^{+1}-I^{+1}\rightarrow H^{+1}_{H^{+1}}\!\!>\!N^{+5}-H^{+1}-I^{+1}$	fall 2·93	rise 6·07	rise 3·14

The core change is calculated from the ionic values in Table IV. The valency change is calculated from the core change and the experimental net result is shown in the last column.

The homopolar relations of the hydrogen halides are as follows :—

$$HCl < HBr < HI,$$

the bond magnetisms being $-4{\cdot}86$, $+4{\cdot}36$, and $+7{\cdot}98$ respectively.

Similarly, for the homopolar nature of the bond between ammonia and hydrogen halide we have

$$NH_3-HCl > NH_3-HBr > NH_3-HI,$$

the bond magnetisms being $+1{\cdot}46$, $-1{\cdot}14$, and $-6{\cdot}07$ respectively. Note, however, that among the hydrogen halides HI has the most homopolar bond, whereas among the ammonium halides NH_4I has the most heteropolar molecular bond.

The above relative order of the polar characters remains the same, whether we adopt the structure $H^{+1}-X^{+1}$ for hydrogen halide or one with a multiple bond.

The use of the single bond involves the core X^{+1} for which, in the isolated state at least, there is a paramagnetic moment unless the ion is in a state somewhat higher than the lowest. Structures with multiple bonds would give non-paramagnetic cores, but as the use of the core X^{+1} as a part of a molecule does not seem to be without some reasonable grounds, it is preferable to adopt the single bond.

The relative order for the polar character of the hydrogen halides agrees with the conclusions of Pauling (Proc. Nat. Acad. Sc. Amer. xiv. pp. 359–362, 1928), and with those of London.

Hydrochlorides of Hydroxylamine, Hydrazine, and Monomethylamine.

The molecular diamagnetisms in this table were determined in this laboratory by Farquharson.

Substance.	Molecular diamagnetism.	Rise in diamagnetism on substitution of group in NH_4Cl.	Diamagnetism lost or gained on substitution.		
			Lost in bonds.	Gained in bonds.	Gained in cores.
NH_4Cl	$35{\cdot}71 \pm 0{\cdot}47$				
NH_2OHHCl ...	$42{\cdot}45 \pm 0{\cdot}39$	6·74	$N^{+5}-H^{+1}$ 7·77	$O^{+2}-H^{+1}$ 3·10 $O^{+2}-N^{+5}$ 7·32	O^{+2} 4·0
NH_2NH_2HCl...	$40{\cdot}90 \pm 0{\cdot}27$	5·19	$N^{+5}-H^{+1}$ 7·77	two $N^{+3}-H^{+1}$ 6·20 $N^{+3}-N^{+5}$ 3·72	N^{+3} 3·0
NH_2CH_3HCl...	$44{\cdot}55 \pm 0{\cdot}39$	8·84	$N^{+5}-H^{+1}$ 7·77	three $C^{+4}-H^{+1}$ 5·01 $C^{+4}-N^{+5}$ 11·45	C^{+4} 0·1

The three substituted ammonium salts are regarded as obtained from NH_4Cl by the substitution of OH, NH_2, and CH_3 respectively, the substituted groups containing the ions O^{+2}, N^{+3}, and C^{+4}. This allows for octet formations round the O, N, and C atoms. The diamagnetisms put for the cores O^{+2}, N^{+3}, and C^{+4} are those given in Table IV.

The diamagnetisms for the bonds N^{+5}--H^{+1}, O^{+2}—H^{+1}, N^{+3}—H^{+1}, and C^{+4}—H^{+1} were obtained from the increments of Table II., which were subjected to appropriate reductions estimated from the magnetic properties of water, ammonia, and methane.

The diamagnetisms for the remaining bonds were obtained by difference from the total experimental rise of diamagnetism observed in each of the three substitutions.

Thus we have for the bonds $O^{+2}-N^{+5}$, $N^{+3}-N^{+5}$, $C^{+4}-N^{+5}$:—the bond diamagnetisms 7·32, 3·72, 11·45 ; depression below increment of Table II. (rise 1·91), 6·82, 17·55 ; relation of homopolar natures of bonds $< <$.

Thus it appears, with regard to homopolar nature, that the bonds of O^{+2}, N^{+3}, and C^{+4} with N^{+5} occupy the same relative position as their bonds with H^{+1}.

From a superficial comparison of the molecular diamagnetisms the hydrochloride of hydrazine does not appear to lie magnetically between those of hydroxylamine and monomethylamine. However, by contrasting the corresponding bonds we have found that the hydrazine salt does occupy an intermediate place.

The substitution of methyl in place of a hydrogen atom of ammonium involves the displacement of one of the $N^{+5}-H^{+1}$ bonds, and it is the one with the highest diamagnetism, namely the 10·54 of Table II. reduced to 7·77 by the activation of valency.

If it is desired to introduce a second methyl group, the four bonds of N^{+5} are again all occupied before substitution, and the $N^{+5}—H^{+1}$ bond to be displaced must again be the one of the highest value, namely 10·54 reduced to 7·77. Accordingly, it is not surprising to find that sometimes successive substitutions of the methyl group in the same ammonium halide give a constant rise of diamagnetism, namely about 8·8 per substituted methyl. In certain cases, however, there is obtained a diamagnetic rise beyond 8·8, which will be discussed in the next section.

The Methyl Substitution Derivatives of Ammonium.

The molecular diamagnetisms in this table were determined in this laboratory, all by Farquharson except the

methyl derivatives of ammonium bromide and of ammonium iodide, which were by Dakers.

Substance.	Molecular diamagnetism.	Difference.	Difference per methyl.
NH_4Cl	35·71±0·47		
		8·84	8·84
$NH_2(CH_3)HCl$	44·55±0·39		
		8·77	8·77
$NH(CH_3)_2HCl$	53·32±0·28		
		10·91	10·91
$N(CH_3)_3HCl$	64·27±0·51		
NH_4Br	46·71±0·36		
		40·50	10·1
$N(CH_3)_4Br$	87·21±0·46		
NH_4I	69·48±0·22		
		35·52	8·88
$N(CH_3)_4I$	105·0 ±0·91		

The substitution of the first methyl group in NH_4Cl produces the same addition of diamagnetism as that of the second methyl, and four times this addition is obtained by the substitution of all the four methyl groups in NH_4I, the average per methyl being the same in the two cases.

If it is supposed that in NH_4Br the addition in diamagnetism obtained by the addition of the first three methyls is $26{\cdot}4$ or $3\times 8{\cdot}8$, then that for the fourth methyl must be $14{\cdot}10$ or $8{\cdot}8+5{\cdot}3$.

The corresponding change in NH_4Cl for the third methyl is $10{\cdot}91$ or $8{\cdot}8+2{\cdot}11$, and for the fourth methyl $8{\cdot}8+x$.

The magnetisms of the molecular bonds in the ammonium halides are $NH_4Cl+1{\cdot}46$, $NH_4Br-1{\cdot}14$, and $NH_4I-6{\cdot}07$.

Difference.....			4·93	4·93
Difference.....	2·60	+	4·93	7·53

The substitution of methyl in NH_4Br raises the diamagnetism by $5{\cdot}3$, whereas the difference in the molecular bonds in NH_4I and NH_4Br is $4{\cdot}93$. Again substitution in NH_4Cl causes a rise of $2{\cdot}11+x$. If we put this equal to $7{\cdot}53$, then x would be $5{\cdot}42$, or about the same as in the fourth substitution in NH_4Br.

The condition of wide polar difference in the molecular bonds of the ammonium halides, in which the bond is most heteropolar in the iodide and least in the chloride, is changed by substitution of methyl into a state in which the chloride

and the bromide are nearly as heteropolar in their molecular bond as the iodide.

The very small diamagnetic addition 8·8, yielded by the substitution of methyl when there is no other addition, is consistent with the very small molecular diamagnetism of methane in which there is displayed a very large fluctuation of angular momentum. The diamagnetic depression below the value for the neutral group is very great for methane, 37·8, compared with that for ammonia, 4·95.

The Chloride, Bromide, and Iodide of Potassium.

The molecules KCl, KBr, and KI have the experimental diamagnetisms $36{\cdot}15 \pm 0{\cdot}36$, $48{\cdot}12 \pm 0{\cdot}85$, and $63{\cdot}9 \pm 0{\cdot}25$ respectively. These figures were measured in this laboratory by Farquharson.

For each of these the molecular diamagnetism is less than the value for the corresponding neutral group, the following depressions being shown :—KCl 9·55, KBr 22·58, KI 32·8.

Compare these with the depressions for the hydrogen halides :—HCl 5·95, HBr 22·55, HI 30·71.

For the hydrogen halides we have already suggested that the fluctuation of angular momentum is very slight in HCl, great in HBr and largest in HI.

Similarly, for the potassium salts the fluctuation is moderate in KCl, larger in KBr, and largest in KI.

The homopolar relations are

$$\begin{array}{ccccc} \mathrm{HCl} & < & \mathrm{HBr} & < & \mathrm{HI} \\ \wedge & & \wedge & & \wedge \\ \mathrm{KCl} & < & \mathrm{KBr} & < & \mathrm{KI}. \end{array}$$

For structures with single bonds K—Cl, K—Br, K—I, the bond magnetisms are −1·26, +4·39, +10·07.

The Halogenates and Perhalogenates of Potassium. Iodic Acid, Periodic Acid, and Iodine Pentoxide.

These substances have the following experimental molecular diamagnetisms :—

$KClO_3$.	$KBrO_3$.	KIO_3.	HIO_3.
$40{\cdot}7 \pm 0{\cdot}47$	$52{\cdot}3 \pm 0{\cdot}49$	$63{\cdot}1 \pm 0{\cdot}50$	$50{\cdot}41 \pm 0{\cdot}30$
$KClO_4$.	KIO_4.	HIO_4.	I_2O_5.
$44{\cdot}6 \pm 0{\cdot}22$	$72{\cdot}0 \pm 0{\cdot}30$	$56{\cdot}55 \pm 0{\cdot}75$	$79{\cdot}4 \pm 0{\cdot}89$

Further, $HIO_3.I_2O_5$ gave $130{\cdot}6 \pm 1{\cdot}40$.

These experimental values were measured in this laboratory by Farquharson, who also carried out a number of other experiments on these substances. The whole of this section will be treated more fully in a subsequent paper.

The Change from Halide to Halogenate.

The change in molecular diamagnetism in passing from KCl to $KClO_3$ is a rise of 4·55 (36·15 to 40·7) ; in passing from KBr to $KBrO_3$ a rise of 4·18 (48·12 to 52·3) ; in passing from KI to KIO_3 a fall of 0·8 (63·9 to 63·1).

When we bear in mind that three oxygen atoms have been added in each case, it is very remarkable that the molecular diamagnetism has been increased by so small an amount in the first two cases and that there is actually a diminution in the third case.

This striking result suggests that the halogen atom in each case undergoes a very large diminution in its diamagnetism caused by the casting off of electrons.

This diminution counteracts to a very large extent the increase due to the addition of three oxygen atoms.

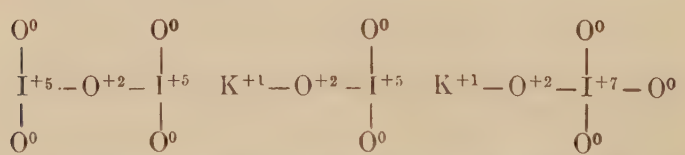
We must reckon also with the change in valency diamagnetism.

The Change from Halogenate to Perhalogenate.

Here the alteration in molecular diamagnetism is not less remarkable than that just described. In passing from $KClO_3$ to $KClO_4$ there is a rise of 3·9 (40·7 to 44·6), and from KIO_3 to KIO_4 a rise of 8·9 (63·1 to 72·0).

The changes brought about in these two cases obviously cannot be represented by the mere addition of one oxygen atom ; there is probably an alteration in the halogen ion.

The following illustrate the structures used in the next section of the discussion :—



We have preferred to use simple structures like these with single bonds, although they involve the use of cores of which O^0 is typical, rather than to use more complicated structures with multiple bonds, even if these allowed the use of cores less liable to be impure diamagnetically in the isolated state.

The following table shows the diamagnetic relations of the halides, halogenates, and perhalogenates :—

Halide to halogenate.	Neutral group.	Diamagnetism of neutral group.	Experimental molec. sus.	Difference.	
KCl	$K^{+1}+Cl^{-1}$	45·7	36·15	− 9·55	
$KClO_3$	$K^{+1}+Cl^{+5}+3O^{-2}$	60·21	40·7	−19·51	
		rise 14·51		fall 9·96	net rise 4·55
KBr	$K^{+1}+Br^{-1}$	70·7	48·12	−22·58	
$KBrO_3$	$K^{+1}+Br^{+5}+3O^{-2}$	68·24	52·3	−15·94	
		fall 2·46		rise 6·64	net rise 4·18
KI	$K^{+1}+I^{-1}$	96·7	63·9	−32·8	
KIO_3	$K^{+1}+I^{+5}+3O^{-2}$	82·18	63·10	−19·08	
		fall 14·52		rise 13·72	net fall 0·80
HI	$H^{+1}+I^{-1}$	80	49·29	−30·71	
HIO_3	$H^{+1}+I^{+5}+3O^{-2}$	65·48	50·41	−15·07	
		fall 14·52		rise 15·64	net rise 1·12
Halogenate to perhalogenate.					
$KClO_3$	$K^{+1}+Cl^{+5}+3O^{-2}$	60·21	40·7	−19·51	
$KClO_4$	$K^{+1}+Cl^{+7}+4O^{-2}$	68·30	44·6	−23·70	
		rise 8·09		fall 4·19	net rise 3·90
KIO_3	$K^{+1}+I^{+5}+3O^{-2}$	82·18	63·10	−19·08	
KIO_4	$K^{+1}+I^{+7}+4O^{-2}$	84·10	72·00	−12·10	
		rise 1·92		rise 6·98	net rise 8·9
HIO_3	$H^{+1}+I^{+5}+3O^{-2}$	65·48	50·41	−15·07	
HIO_4	$H^{+1}+I^{+7}+4O^{-2}$	67·40	56·55	−10·85	
		rise 1·92		rise 4·22	net rise 6·14

The simplest structure of I_2O_5 contains six single bonds which show a paramagnetism of +8·81. This marked homopolar character is retained in the internal bonds of the complex anion of iodic acid.

The hydration of one molecule of I_2O_5 gives two molecules of iodic acid which contain eight bonds which show a diamagnetism of −8·52. The three iodine-oxygen bonds of each acid molecule have their homopolar character masked by the strong heteropolar nature of the fourth bond—the one connecting to the simple cation.

The magnetic relations of the complete hydration are as follows :—

	H_2O	+ I_2O_5	→ $2HIO_3$.	Diamagnetic rise.
Mol. sus.	−12·96	−79·4	−100·82	8·46
Bonds	2	6	8	
Bond magnetisms ...	−8·87	+8·81	−8·52	8·46

The rise in diamagnetism on hydration is therefore due to the formation of bonds of marked heteropolar nature. The hydration takes place in stages, thus :—

			Diamagnetic rise.
	$H_2O+3I_2O_5$	→ $2(HIO_3 . I_2O_5)$	10·06
	$2H_2O+2(HIO_3 . I_2O_5)$	→ $6HIO_3$	15·34
Total result...	$3H_2O+3I_2O_5$	→ $6HIO_3$	25·40 or 3×8·46

Magnetisms of Bonds of Halogenates and Perhalogenates.

	$KClO_3$.	$KBrO_3$.	KIO_3.	HIO_3.
Number of bonds	4	4	4	4
Magnetism of bonds ...	+0·18	−3·39	−0·25	−4·26
	$KClO_4$.		KIO_4.	HIO_4.
Number of bonds	5		5	5
Magnetism of bonds ...	−1·04		−12·64	−13·89

A contrast of the KIO_3 and HIO_3 shows that the single bond attached to H^{+1} is more heteropolar than that to K^{+1}; and the same holds for KIO_4 and HIO_4.

The iodine-oxygen bonds are very homopolar, but the chlorine-oxygen bonds are more so. Accordingly, the three internal bonds in the complex anion are more homopolar in the chlorate than in the iodate of potassium. A similar contrast is obtained with $KClO_4$ and KIO_4, and with $KClO_3$ and $KBrO_3$. On the other hand, $KBrO_3$ does not lie magnetically between $KClO_3$ and KIO_3.

The weakening of the homopolar nature of the halogen-oxygen bond, caused by the raising of the positive valency of the halogen, is displayed by a contrast of $KClO_3$ and $KClO_4$, of KIO_3 and KIO_4, and of HIO_3 and HIO_4. Indeed, the diamagnetism of the bond is so strong in the periodates that the more homopolar aspect of I_2O_5 is changed into one more heteropolar.

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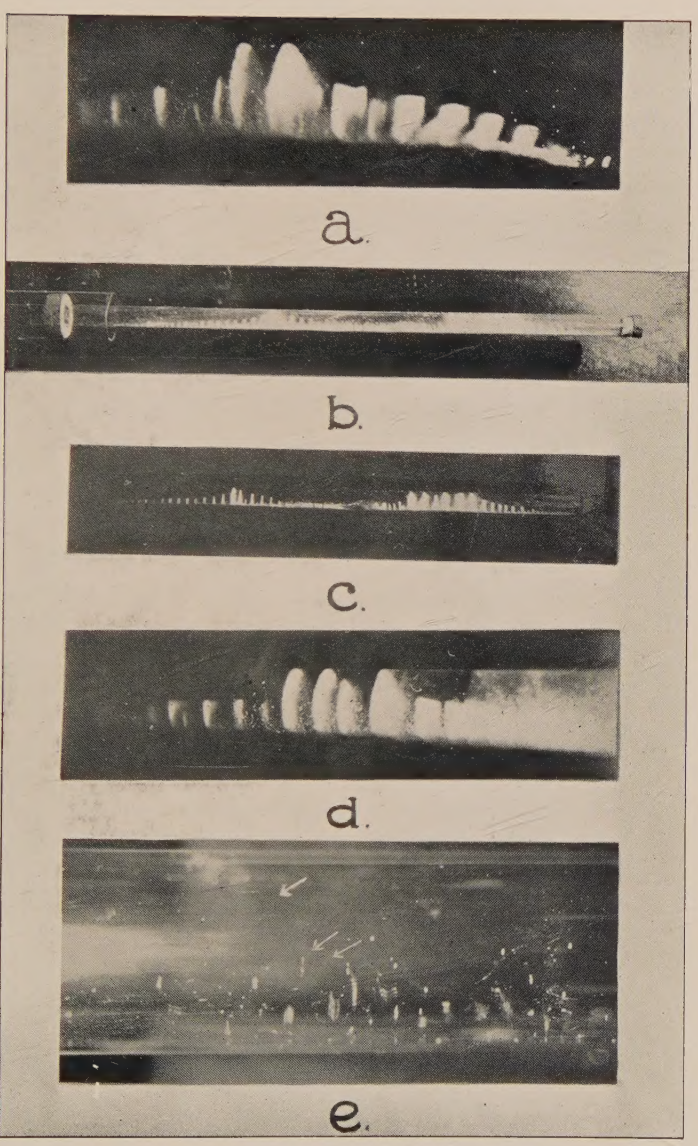
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]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